

Calculate Phase and Chemical Equilibria Using Process Safety Office[®] SuperChems Expert[™]



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IO MOSAIC CORPORATION

**Calculate Phase and Chemical Equilibria
Using Process Safety Office[®] SuperChems
Expert[™]**

Process Safety and Risk Management Practices

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Contents

1	Introduction	2
2	Historical Perspective	2
3	Minimization Algorithm	3
4	Simultaneous Chemical and Physical Equilibrium	3
5	Physical Equilibrium	4
6	Atom Matrix Rank Calculation	5
7	Standard Gibbs Free Energy Data	6
8	Calculation of the Chemical Potential μ	7
9	Thermodynamic Stability Criteria	8
10	Phase Splitting and Coalescence	8
11	Liquid-liquid Equilibrium	9
12	Case Studies	10
12.1	Ideal Vapor Phase Chemical Equilibrium	10
12.2	Nonideal Two-phase Chemical Equilibrium	10
12.3	Nonideal Three-phase Physical Equilibrium	13
12.4	Nonideal Two-phase Physical Equilibrium	13
12.5	Nonideal Two-phase Chemical Equilibrium	14
13	Conclusions	15
A	Chemical-Physical Equilibrium Equations	17
B	Physical Equilibrium Equations	18

1 Introduction

Direct minimization of the Gibbs free energy can be used to calculate phase equilibria, chemical equilibria, and/or simultaneous physical and chemical equilibria. This method may be preferred for systems where multiple liquid phases can coexist and/or where retrograde phase behavior is possible during depressuring or pressure relief.

Some of the advantages of direct minimization of the Gibbs free energy include:

1. The atom matrix can be constrained to ensure that inert liquids and/or inert gases are only present in their respective phases. For example, this can be useful for systems containing hydrogen and heavy polymers.
2. The atom matrix can be constrained to ensure partial or user defined conversion of one or more chemical species.
3. Multiple liquid, vapor, and solid phases can be handled simultaneously with simplicity.
4. Phase splitting can be determined a priori.

Some of the disadvantages include:

1. The Gibbs free energy minimum can be very flat and requires high precision estimates.
2. The Formation energies of all chemical species have to be thermodynamically consistent and calculated at the system temperature using reference elements.
3. Reasonable initial guesses for phase splitting are required. Normally, the most non-ideal liquid component in the mixture will likely form the dominant component in one liquid phase while the second most non-ideal liquid component will likely form the dominant component in the second liquid phase.

2 Historical Perspective

Brinkley [1, 2] laid the foundations to a general-purpose algorithm for the computation of chemical equilibria in 1947. His algorithm addressed simple ideal systems and was intended for use with hand calculators, although the algorithm did lend itself to implementation on computers.

In 1958, White et al. [3] and G. B. Dantzig [4], working at the Rand Corporation, developed an algorithm that solved the chemical equilibrium problem by the direct minimization of the Gibbs free energy. They were probably the first to use the concept of nonlinear optimization to solve the problem. They used Newton's method to minimize the Gibbs free energy of an ideal system. Boyton [5] and Oliver et al. [6] extended the Rand algorithm to handle pure solid species, and Dlugniewski and Adler [7] extended it to handle mixed phases.

Gordon and McBride [8] working at the NASA Lewis Research Center, developed an algorithm that was similar to the Rand algorithm. This algorithm also addressed simple ideal systems, as this was justified by the high temperature systems encountered in rocket technology.

Probably, the first to implement nonideal models for the solution of complex equilibria were George et al. [9]. They used Powell's method to minimize the Gibbs free energy. In order to avoid singularities they had to transform the variables and eliminate the constraints by introducing allocation functions.

Gautam and Seider [10], working for the U.S. Department of Energy (the ASPEN Project), used the quadratic programming method of Wolfe to extend the Rand algorithm. Their algorithm handled nonideal systems, pure solid species and electrolytic solutions. They also developed a new phase splitting algorithm to determine the number of phases and their associated composition at equilibrium. Their algorithm is perhaps the most widely accepted algorithm and was implemented in the early versions of the ASPEN process simulator.

3 Minimization Algorithm

The computation of the equilibrium state of a system is one of constrained optimization. The minimization of the Gibbs free energy is subject to mass, element balance constraints, and where applicable, user defined constraints. Recent advances in the field of nonlinear optimization have greatly simplified the solution of this problem. Process Safety Office[®] SuperChems Expert[™] component uses the Wilson-Han-Powell successive quadratic programming (SQP) algorithm to directly minimize the Gibbs free energy for nonideal multiphase systems. Advantages of this algorithm include its low number of function and gradient evaluations and its ability to handle simple bounds on variables, such as non-negativity constraints which eliminates the need to transform variables in order to avoid singularities.

Cubic equations of state are an attractive choice for representing nonideal systems. They can be solved analytically without iterative procedures. The Melhem [11, 12] modification of the Peng-Robinson equation of state (MMPR) provides several advantages when used in the direct minimization of the Gibbs free energy for nonideal multiphase system including a better temperature dependency form, a composition dependent mixing rule, analytic derivatives, and the a priori calculation of thermodynamic phase stability.

4 Simultaneous Chemical and Physical Equilibrium

Mathematically, the equilibrium problem is to minimize the total Gibbs free energy

$$G^t = \sum_{i=1}^S n_i \frac{G_i^o}{RT} + \sum_{i=1}^{N-S} \sum_{p=1}^{\pi} n_{ip} \left[\frac{G_i^o}{RT} + \ln \left(P \phi_{ip} \frac{n_{ip}}{n_{Tp}} \right) \right] \quad (1)$$

subject to the equality constraints,

$$\sum_{i=1}^S a_{ki}n_i + \sum_{i=1}^{N-S} \sum_{p=1}^{\pi} a_{kip}n_{ip} = b_k \quad k = 1, \dots, R \quad \equiv C_1 \quad (2)$$

and the inequality constraints,

$$n_i \geq 0 \quad i = 1, \dots, S, \dots, N\pi \quad \equiv C_2 \quad (3)$$

where N the number of chemical species, π is the number of phases, S is the number of condensed solid species, n_{ip} is the equilibrium number of moles of the i th species in phase p , n_{Tp} is the total number of moles in phase p , G_i^o is the standard Gibbs free energy of the i species evaluated at the system temperature T , P is the system pressure, a_{ki} is the number of atoms of element k in species i , b_k is the number of gram-atoms of element k , and R is the rank of the atom matrix (usually equal to the number of elements). The element abundance vector \mathbf{b} is calculated as the product of the atom matrix \mathbf{A} and the initial number of moles \mathbf{n}^o

$$\mathbf{A}\mathbf{n}^o = \mathbf{b} \quad (4)$$

The number of variables NVAR is equal to $((N - S) \times \pi + S)$, the number of equality constraints NMEQ is equal to the rank of the atom matrix R and the total number constraints NCON is equal to $(\text{NVAR} + \text{NMEQ})$.

5 Physical Equilibrium

For the case without chemical reactions, an atom balance is not required and the function minimized becomes:

$$\Delta G^t = \frac{G^t - \sum_{i=1}^N n_i^o G_i^o}{RT} = \sum_{i=1}^N \sum_{p=1}^{\pi} n_{ip} \left[\ln \left(P \phi_{ip} \frac{n_{ip}}{n_{Tp}} \right) \right] \quad (5)$$

subject to the equality constraints

$$n_i^o - \sum_{p=1}^{\pi} n_{ip} = 0 \quad \equiv C_1 \quad i = 1, \dots, N \quad (6)$$

and the inequality constraints

$$n_i^o \geq n_{ip} \geq 0 \quad \equiv C_2 \quad (7)$$

where n_i^o is the initial number of moles of the i th species.

The number of variables NVAR is equal to $(N \times \pi)$, the number of equality constraints NMEQ is equal to the number of species N and the total number constraints NCON is equal to $(\text{NVAR} + \text{NMEQ})$.

6 Atom Matrix Rank Calculation

Singular value decomposition (SVD) is the preferred method [13] to calculate the rank, R , of the atom matrix. Several unique characteristics of the singular value decomposition are worth mentioning. Singular value decomposition is often used to solve the linear system $AX = B$. A is an $[m, n]$ matrix where m is usually greater or equal to n . X is the solution vector of size $[n, 1]$. B is the right hand side vector of size $[m, 1]$.

$$\mathbf{A} = \mathbf{U}\mathbf{W}\mathbf{V}^T \text{ and } \mathbf{A}^T = \mathbf{V}\mathbf{W}\mathbf{U}^T \quad (8)$$

The two matrices U and V are each orthogonal, or in other words, their columns are orthonormal. U is of size $[m, n]$ and V is of size $[n, n]$. W is a diagonal matrix of size $[n, n]$ and is usually stored as a vector of size $[n]$. W always contains positive or zero (singular) values. We note that:

$$\mathbf{U}^T\mathbf{U} = \mathbf{V}^T\mathbf{V} = \mathbf{I} \text{ and} \quad (9)$$

$$\mathbf{X} = \mathbf{V} \times (\mathbf{1}/\mathbf{W}) \times \mathbf{U}^T \times \mathbf{B} \quad (10)$$

For a square A matrix:

$$\mathbf{A}^{-1} = \mathbf{V} \times (\mathbf{1}/\mathbf{W}) \times \mathbf{U}^T \quad (11)$$

When A is a square singular matrix, W will contain zero elements. If A is ill-conditioned or near singular, W will contain very small numbers or numbers close to the machine precision. For a singular A matrix and where the right hand vector B is zero, SVD yields multiple solutions. Any V column whose corresponding W_j (element j) is zero yields a solution. When B is not zero, one might want to select the X solution vector that has the smallest length $|X|^2$. In this case, replace the value of $1/W_j$ where $W_j = 0$ by 0.

For cases where m is less than n , a unique solution is not expected. The SVD has to yield at least $n - m$ zeros or very small W_j values. Depending on the number of atoms and the number of components, additional zeros in W are possible. The columns of V corresponding to the zero elements of W are the basis vectors whose linear combinations with a particular solution, span the solution space. Each one of those columns represents the stoichiometry of an independent chemical reaction.

When the number of equations is more than the number of unknowns ($m > n$), SVD can directly yield the least-squares solution. The least squares solution vector is given by Equation 10. In general, where m is larger than n , W will not be singular.

In cases where most of the elements of W are either zeros or close to the machine precision, A can be approximated by a few terms in the sum below:

$$A_{ij} = \sum_{k=1}^n W_k U_{ik} V_{jk} \quad (12)$$

As a result, only the columns of U and V that correspond to non-zero values of W elements need to be stored in order to recover or approximate the A matrix.

For direct minimization of the Gibbs free energy, the atom matrix is first decomposed into the three matrices, U , V , and W :

$$\mathbf{A} = \mathbf{U}\mathbf{W}\mathbf{V}^T \quad (13)$$

If the rank of the matrix is less than the number of elements, the dependent rows corresponding to the zero elements of the diagonal vector \mathbf{W} are eliminated from the atom matrix. The number of independent chemical reactions is equal to $C = n - R$. The C independent, but non-unique stoichiometric vectors are given by the columns of \mathbf{V} corresponding to the zero elements of the \mathbf{W} vector.

This method has a number of advantages. Linear stoichiometric constraints can easily be incorporated into the atom matrix using a procedure similar to that outlined by Smith and Missen [14]. This method also handles the presence of isomers without modifications to the atom matrix.

Consider the system ethylene, water, ethyl alcohol and dimethyl ether [15] where the alcohol and ether are isomers. With $m = 3$ and $n = 4$, the atom matrix is:

$$\begin{bmatrix} & \text{H}_2\text{O} & \text{C}_2\text{H}_4 & \text{C}_2\text{H}_5\text{OH} & \text{C}_2\text{H}_6\text{O} \\ \text{C} & 0 & 2 & 2 & 2 \\ \text{H} & 2 & 4 & 6 & 6 \\ \text{O} & 1 & 0 & 1 & 1 \end{bmatrix} \quad (14)$$

Since the last two columns are the sum of the first two, the rank calculated is 2 and the number of independent reactions is $C = n - R = 2$. The calculated stoichiometry of the two independent chemical reactions are obtained from the V columns corresponding to the zero W elements:

$$\nu^T = \begin{bmatrix} 0.632 & 0.632 & -0.316 & -0.316 \\ 0.000 & 0.000 & -0.707 & 0.707 \end{bmatrix} \quad (15)$$

which corresponds to the following two (non-unique) reactions,



Reaction stoichiometry is an important mass balance constraint. This constraint can be modified or augmented based on calorimetry measurements to further constrain the yield or conversion of one or more of all the possible thermodynamically feasible reactions.

7 Standard Gibbs Free Energy Data

A temperature dependent value of G_i^o is required for chemical equilibrium estimates. In our implementation of the direct minimization of the Gibbs free energy, G_i^o is calculated for species i from the formation reaction of species i from its chemical elements. Note that the formation energies of the chemical elements are usually zero and must to be thermodynamically consistent with the formation energies of the species being formed.

The formation reaction standard free energy data is calculated from the equilibrium constant K which in turn is calculated from heat capacity data and standard heats and free energies of formation data. The formation reaction equilibrium constant is related to the standard free energy of reaction by:

$$G_i^o(T) = -RT \ln K_i = \sum_{j=1}^M \nu_j G_{j,F}(T) \quad (18)$$

where M is the number of elements plus one and ν_j is the stoichiometric coefficient of element j or species i in the formation reaction of species i .

8 Calculation of the Chemical Potential μ

The chemical potential, μ_{ip} , of the i th species in a multicomponent mixture is given by:

$$\mu_{ip} = G_i^o + RT \ln \frac{\hat{f}_{ip}}{f_i^o} \quad (19)$$

where $f_i^o = 1$ and the fugacity \hat{f}_{ip} is related to the mole fraction of the i th component in the mixture by:

$$\hat{f}_{ip} = \phi_i^p P x_{ip} \quad (20)$$

where ϕ_i^p is the fugacity coefficient and is a function of T , P , and the number of moles of the i th component in the mixture. Thus,

$$\mu_{ip} = G_i^o + RT \ln \left(P \phi_i^p \frac{n_{ip}}{n_{Tp}} \right) \quad (21)$$

where $n_{Tp} = \sum n_{ip}$, the total number of moles in the p th phase.

The fugacity coefficient and its derivative are calculated analytically from the MMPR equation of state [11, 12]. This method has several advantages over the use of traditional activity coefficients including but not limited to:

1. The activity coefficient model can only approximate nonideality in the liquid phase. An equation of state is still required for the vapor phase.
2. Activity coefficient models give poor results for systems at high pressure and systems containing supercritical compounds.

The fugacity coefficient ϕ_i and its derivatives are obtained directly from the MMPR.

9 Thermodynamic Stability Criteria

We can determine a priori when a mixture is mechanically and/or diffusonally stable if we can obtain thermodynamic expressions for the chemical potential μ from a suitable equation of state. The stability criteria can be stated as follows (see [16]):

1. The necessary and sufficient condition for thermodynamic stability in an N component system is,

$$y_{kk}^{(k-1)} > 0 \quad k = 1, 2, \dots, (N + 1); \quad (22)$$

2. All points on the limit of stability obey,

$$y_{(N+1)(N+1)}^{(N)} = 0 \quad (23)$$

where in thermodynamic notation,

$$y_{11}^0 = \frac{T}{C_v} > 0 \quad (24)$$

$$y_{22}^1 = - \left(\frac{\partial P}{\partial V} \right)_{T, n_j} > 0 \quad (25)$$

$$y_{33}^2 \cdots y_{(N+1)(N+1)}^{(N)} = \begin{vmatrix} \left(\frac{\partial \mu_1}{\partial n_1} \right)_{T, P, n_j} & \cdots & \left(\frac{\partial \mu_1}{\partial n_{(N-1)}} \right)_{T, P, n_j} \\ \vdots & \vdots & \vdots \\ \left(\frac{\partial \mu_{(N-1)}}{\partial n_1} \right)_{T, P, n_j} & \cdots & \left(\frac{\partial \mu_{(N-1)}}{\partial n_{(N-1)}} \right)_{T, P, n_j} \end{vmatrix} > 0 \quad (26)$$

where

$$\left(\frac{\partial \mu_i}{\partial n_j} \right)_{T, P, n_i} = RT \left[\frac{\partial \ln \phi_i}{\partial n_j} + \frac{1}{n_i} \frac{\partial n_i}{\partial n_j} - \frac{1}{n_T} \right] \quad (27)$$

The use of these criterion is simple as analytic derivatives for all terms are available (see [11, 12]). Equations 24 and 25 represent the locus of points on the binodal curve and the determinant in equation 26 represents the locus of points on the spinodal curve. If all criterion are positive then the mixture is stable, and if any of the terms are zero then the mixture is metastable or at its limit of stability. If any of the criterion is negative then the mixture is unstable and a presence of an additional phase is indicated. If equations 24 or 25 is negative the mixture is said to be mechanically unstable (usually high temperature systems) and if the determinant is negative the the mixture is said to be diffusonally unstable.

10 Phase Splitting and Coalescence

One of the frequently encountered problems in multiphase equilibrium is the determination of the number of phases and their relative molar distribution at equilibrium. One method is to assume

Table 1: Experimental Liquid-Liquid Miscibility Limits [18, 19]

System	ID	T, [K]	P, [atm]	x_1^I	x_1^{II}
Butanol-Water	1	365	1.0	0.260	0.045
Isobutanol-Water	2	364	1.0	0.335	0.055
Methyl ethyl ketone-Water	3	346	1.0	0.640	0.045
Ethyl acetate-Water	4	343	1.0	0.700	0.180
Methanol-Hexane	5	323	1.0	0.885	0.155

the maximum number of phases at equilibrium, as given by the phase rule. However, due to the fixed nature of the constraints of temperature and pressure, the phase rule does not always give the accurate number of phases at equilibrium. The most popular method is to split a phase into two trial phases and test to see whether a decrease in the Gibbs free energy is observed over a number of iterations. But, this procedure can be rather time-consuming and expensive for multicomponent/multiphase systems.

In order to overcome these problems, the stability criterion outlined by Beegle et al [17] and Heidemann [16], as outlined earlier, is used to determine, a priori, the feasibility of an additional phase.

The use of the above outlined stability criterion make the phase splitting algorithm simple. The minimization is carried out for the phases specified by the user. After convergence, the stability criterion is applied to each of the phases. If any of the criterion are violated, an additional phase is added (usually Liquid). However, if the total number of moles of any phase is below a predetermined tolerance, that phase is deleted.

For supercritical systems, additional checks are performed to confirm if the converged phase solutions are vapor or liquid. In the case where a converged solution for multiple phases yields the same compositions, the phases are coalesced. Converged solutions for each unique phase are also checked for consistency. Depending on the final conditions, a vapor phase may be re-classified as a liquid phase and coalesced with a liquid phase and vice versa. This is highly dependent on the MMPR compressibility factor and pseudo critical properties estimates.

11 Liquid-liquid Equilibrium

The use of the stability criterion outlined above is illustrated in predicting liquid-liquid miscibility limits. Table 1 lists the experimental values for the miscibility limits for five mixtures and Table 2 gives the calculated results as well as the binary interaction parameters used for the MMPR equation of state. As shown, the miscibility limits predicted by the stability criterion are accurate.

Table 2: Calculated Miscibility Limits Using Stability Analysis Criterion

ID	K_{12}	K_{21}	x_1^I	x_1^{II}
1	-0.08891	-0.11033	0.2871	0.0502
2	-0.10760	-0.12039	0.2577	0.0582
3	-0.14961	-0.18254	0.6510	0.0898
4	-0.16851	-0.22598	0.5216	0.0539
5	0.08755	0.19134	0.7554	0.2748

12 Case Studies

SuperChems Expert was tested on a number of case studies. The SuperChems Expert algorithm automatically scales the objective function and constraints. A convergence tolerance of 1.0×10^{-8} kmol was used for all the case studies.

12.1 Ideal Vapor Phase Chemical Equilibrium

SuperChems Expert was tested for the steam reforming system described by White and Seider. This gas phase chemical equilibrium problem takes place at $1067^\circ K$ and 1.235 MPa (12.19 atm) with the following reaction:



Nitrogen is also present in the system as an inert. Under these conditions, the gas mixture can be assumed to behave ideally. No interaction parameters were used in the MMPR equation of state. Initial compositions and compositions computed at equilibrium by this work and those reported by White and Seider are shown in Table 3. The guessed composition for each species was set to 1.0×10^{-3} . The stability analysis algorithm reported the phase to be stable with the following stability criterion values:

$$-\left(\frac{dP}{dV}\right) = 1.3204 \times 10^{-5}$$

$$\text{Stability Determinant} = 2.5521 \times 10^{11}$$

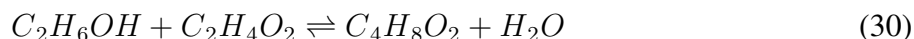
12.2 Nonideal Two-phase Chemical Equilibrium

Ethanol and acetic acid are esterified to ethyl acetate and water at $358.2^\circ K$ and 1.0 atm. This two phase chemical equilibrium problem was originally solved by Sanderson and Chien, and subsequently by George et al. and Gautam and Seider. Sanderson and Chien report a split of 63.01%

Table 3: Problem 1: Solution

Species	Initial composition	Solution by White and Seider	Solution by this work
CH ₄	15.14	0.875	0.886
H ₂ O	84.07	61.821	61.860
N ₂	0.59	0.590	0.590
H ₂	0.20	50.980	50.917
CO	0	6.282	6.298
CO ₂	0	7.983	7.956

vapor and 36.99% liquid. George et al proved that these values obtained by Sanderson and Chein to be inconsistent as they did not satisfy the chemical reaction constraints. The equilibrium values obtained by these authors are shown in Table 4. The reaction taking place is:



with an equimolar initial mixture of ethanol and acetic acid. Since this is a fairly nonideal system, binary interaction parameters were regressed from binary VLE data. The following values were used:

$$k_{ij} = \begin{bmatrix} 0.0 & -0.0911 & -0.1690 & -0.1400 \\ -0.0911 & 0.0 & 0.0319 & -0.0315 \\ -0.1690 & 0.0319 & 0.0 & -0.0218 \\ -0.1400 & -0.0315 & -0.0218 & 0.0 \end{bmatrix} \quad (31)$$

$$l_{ij} = \begin{bmatrix} 0.0 & 0.0500 & 0.226 & 0.0604 \\ -0.0500 & 0.0 & 0.0389 & 0.0072 \\ -0.226 & -0.0389 & 0.0 & -0.0155 \\ -0.0604 & -0.0072 & 0.0155 & 0.0 \end{bmatrix} \quad (32)$$

where (i, j) = water, ethanol, ethyl-acetate and acetic acid. This problem was solved using two different guesses. In the first run, a guess of 1.0×10^{-3} was used for all the species in all phases. In the second run, a guess of 1, 49, 1, 49 for water, ethanol, acetate and acid respectively, was used for the vapor phase and 1.0×10^{-3} for all species in the liquid phase. The results obtained by both runs are given in Table 5. Also shown are the stability analysis data and the minimum obtained at equilibrium for both runs. As expected, convergence was achieved faster when guesses were provided for the components in each phases. However, the minimum obtained for each case was the same.

Table 4: Literature reported values for Example 2

Species	Initial	Sanderson and Chien		George et al		Gautam and Seider	
		Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
H ₂ O	0	16.9205	10.2965	42.4642	< 10 ⁻⁸	42.4639	0.0
C ₂ H ₆ O	50	15.9954	6.7876	7.5353	< 10 ⁻⁸	7.5361	0.0
C ₄ H ₈ O	0	22.1756	5.0415	42.4642	< 10 ⁻⁸	42.4639	0.0
C ₂ H ₄ O ₂	50	7.9204	14.8625	7.5353	< 10 ⁻⁸	7.5361	0.0
Total	100	63.01	36.99	100.0	< 10 ⁻⁸	100.0	0.0

Table 5: Solution to Example 2

Species	Solution 1 [†]		Solution 2 [‡]	
	Vapor	Liquid	Vapor	Liquid
H ₂ O	42.1012	0.2975	42.4637	0.00001
C ₂ H ₆ O	7.5742	0.0272	7.5363	< 10 ⁻⁶
C ₄ H ₈ O	42.3349	0.0637	42.4637	< 10 ⁻⁶
C ₂ H ₄ O ₂	7.4716	0.1298	7.5363	< 10 ⁻⁶
Total	99.4819	0.5181	99.99998	0.000021
$-(dP/DV)$	3.42×10^{-7}	5.38×10^2	3.40×10^{-7}	1.01×10^7
Stability Det.	2.01×10^3	9.12×10^{10}	2.00×10^3	2.80×10^{24}
G_{min}/RT		-1.74201		-1.74201

† Solution with no guesses.

‡ Solution with guesses.

Table 6: Solution to Example 3

Species	2 Phases		3 Phases		
	Vapor	Liquid	Vapor	Liquid 1	Liquid 2
C ₄ H ₁₀ O	< 10 ⁻⁸	0.3	< 10 ⁻⁸	0.2931	0.0069
H ₂ O	< 10 ⁻⁸	0.7	< 10 ⁻⁸	0.2955	0.4045
Total	< 10 ⁻⁸	1.0	< 10 ⁻⁸	0.5886	0.4114
-(dP/dV)	1.61 × 10 ³	3.47 × 10 ²	1.71 × 10 ³	3.13 × 10 ²	4.29 × 10 ³
Stability det.	3.72 × 10 ¹⁰	-7.72	3.53 × 10 ¹⁰	3.28 × 10 ²	5.15 × 10 ⁴
G _{min} /RT	-1.0111		-1.0243		

12.3 Nonideal Three-phase Physical Equilibrium

A mixture of 0.3 mol n-butanol and 0.7 mol water is flashed at 355°K and 1.0 atm. This system is known to split into two liquid phases under these conditions. This simple flash problem illustrates the phase splitting algorithm. The following binary interaction parameters were used:

$$k_{ij} = \begin{bmatrix} 0.0 & -0.088799 \\ -0.088799 & 0.0 \end{bmatrix} \quad (33)$$

$$l_{ij} = \begin{bmatrix} 0.0 & -0.11039 \\ 0.11039 & 0.0 \end{bmatrix} \quad (34)$$

where, (i, j) = n-butanol, water. The minimization calculation was started by assuming two phases, a vapor and liquid phase. After 3 iterations, the algorithm converged to an answer the results of which are shown in Table 6. At this point, as the stability determinant for the liquid phase was negative, the phase splitting algorithm concluded that the phase was unstable and automatically restarted the calculations by adding an additional liquid phase. The results are given in Table 6. At equilibrium, the vapor phase is non-existent. It was, however, not necessary to eliminate this phase at any stage of the calculations as the algorithm does not have any problems in handling near zero flow rates.

12.4 Nonideal Two-phase Physical Equilibrium

A seven component mixture containing propylene, diisopropyl-ether, isopropanol, water, acetone, hexene and n-propanol is flashed at 388.5°K and 40.8 atm. This two phase equilibrium problem was solved by Gautam and Seider. The results obtained by them and by this work are shown in

Table 7: Solution to Example 4

Species	Initial	Gautam and Seider		This work	
		Vapor	Liquid	Vapor	Liquid
Propylene	78.00	77.9805	0.0195	77.9918	0.0082
IPE	2.14	2.1384	0.0016	2.1141	0.0259
IPA	5.06	4.6382	0.3827	4.7571	0.3029
Water	11.90	4.0035	7.8965	5.7613	6.1387
Acetone	0.071	0.0671	0.0039	0.0703	0.0007
Hexene	2.80	2.7999	0.00001	2.7999	0.00002
n-Propanol	0.03	0.0284	0.0016	0.0262	0.0038

Table 7. The following partial list of binary interaction parameters were used for this system:

$$k_{ij} = \begin{bmatrix} 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.04402 & -0.222 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.04402 & 0.0 & -0.152 & 0.03401 & 0.0 & -0.00675 \\ 0.0 & -0.222 & -0.152 & 0.0 & -0.096 & 0.0 & -0.11374 \\ 0.0 & 0.0 & 0.03401 & -0.096 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & -0.00657 & -0.11347 & 0.0 & 0.0 & 0.0 \end{bmatrix} \quad (35)$$

$$l_{ij} = \begin{bmatrix} 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & -0.053 & -0.412 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.053 & 0.0 & -0.0707 & 0.01832 & 0.0 & -0.0022 \\ 0.0 & 0.412 & 0.0707 & 0.0 & 0.172 & 0.0 & 0.03466 \\ 0.0 & 0.0 & -0.01832 & -0.172 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 \\ 0.0 & 0.0 & 0.0022 & -0.03466 & 0.0 & 0.0 & 0.0 \end{bmatrix} \quad (36)$$

where, $(i, j) =$ propylene, IPE, IPA, water, acetone, hexene and n-propanol. A partial list was used due to the availability of binary VLE data for only some systems. Regardless of this limitation, the results compare favorably with those reported by Gautam and Seider.

12.5 Nonideal Two-phase Chemical Equilibrium

Benzene and hydrogen are reacted at $500^\circ K$ and 30 atm to form cyclohexane:



for an initial composition containing 1.0, 3.07 and 0.2 moles benzene, hydrogen and cyclohexane respectively. This two phase chemical equilibrium problem is taken from Henley and Rosen. The

Table 8: Solution to Example 5

Species	Initial (kmol)	Vapor (kmol)	Liquid (kmol)
C ₆ H ₆	1.00	0.000002	0.000007
H ₂	3.07	0.053742	0.016287
C ₆ H ₁₂	0.20	0.172855	1.027136
Total	4.27	0.226599	1.043431

binary interaction parameters used were:

$$k_{ij} = \begin{bmatrix} 0.0 & -2.62717 & 0.02413 \\ -2.62717 & 0.0 & -2.95736 \\ 0.02413 & -2.95736 & 0.0 \end{bmatrix} \quad (38)$$

$$l_{ij} = \begin{bmatrix} 0.0 & -0.55343 & -0.00211 \\ 0.55343 & 0.0 & 0.66357 \\ 0.00211 & -0.66357 & 0.0 \end{bmatrix} \quad (39)$$

A guess of 1.0×10^{-3} was used for all components in all phases. The results obtained are shown in Table 8.

13 Conclusions

The stream utilities in SuperChems Expert were upgraded to enable the user to select direct minimization of the Gibbs free energy as a method for performing vapor/liquid/liquid/solid equilibrium calculations instead of the standard flash routines default. This new option is available for isothermal flash calculations, constant volume calculations, user defined vapor quality calculations, and also for stream flow calculations using either an isentropic or isenthalpic thermodynamic path. The standard flash routines were also upgraded to enable solids handling and vapor/liquid/solid equilibrium calculations. These enhancements are very useful when dealing with highly nonideal systems phase equilibrium and/or when dealing with multiple liquid phases with/without chemical equilibrium.

How can we help?

In addition to our deep experience in process safety management (PSM) and the conduct of large-scale site wide relief systems evaluations by both static and dynamic methods, we understand the many non-technical and subtle aspects of regulatory compliance and legal requirements. When you work with ioMosaic you have a trusted ISO certified partner that you can rely on for assistance and support with the lifecycle costs of relief systems to achieve optimal risk reduction and PSM compliance that you can evergreen. We invite you to connect the dots with ioMosaic.

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A Chemical-Physical Equilibrium Equations

The number of variables, equality constraints and total number of constraints are,

$$\text{NVAR} = S + (N - S)\pi$$

$$\text{NMEQ} = R$$

$$\text{NCON} = \text{NVAR} + \text{NMEQ}$$

The objective function is,

$$G^t = \sum_{i=1}^S n_i \frac{G_i^o}{RT} + \sum_{i=1}^{N-S} \sum_{p=1}^{\pi} n_{ip} \left[\frac{G_i^o}{RT} + \ln \left(P \phi_{ip} \frac{n_{ip}}{n_{Tp}} \right) \right]$$

and the constraints are,

$$C_1 \equiv \sum_{i=1}^S a_{ki} n_i + \sum_{i=1}^{N-S} \sum_{p=1}^{\pi} a_{ki} n_{ip} = b_k \quad k = 1, \dots, \text{NMEQ}$$

$$C_2 \equiv n_i \geq 0 \quad i = 1, \dots, \text{NVAR}$$

The gradient of the objective function and the constraints are,

1. For $0 < i \leq S$,

$$\frac{\partial G^t}{\partial n_i} = \frac{G_i^o}{RT}$$

and

$$\frac{\partial C_1}{\partial n_i} \equiv a_{ki} \quad k = 1, \dots, \text{NMEQ}$$

$$\frac{\partial C_2}{\partial n_i} \equiv 1$$

2. For $S < ip \leq \pi(N - S)$, and $p = 1, \dots, \pi$

$$\frac{\partial G^t}{\partial n_{ip}} = \frac{G_i^o}{RT} + \ln \left(P \phi_i^p \frac{n_{ip}}{n_{Tp}} \right) + \sum_{j=1}^{N-S} n_{jp} \left[\frac{\partial \ln \phi_j^p}{\partial n_{ip}} + \frac{\partial n_{jp}}{\partial n_{ip}} \frac{1}{n_{jp}} - \frac{1}{n_{Tp}} \right]$$

and

$$\frac{\partial C_1}{\partial n_{ip}} \equiv a_{ki} \quad k = 1, \dots, \text{NMEQ}$$

$$\frac{\partial C_2}{\partial n_{ip}} \equiv 1$$

B Physical Equilibrium Equations

The number of variables, equality constraints and total number of constraints are,

$$\text{NVAR} = N\pi$$

$$\text{NMEQ} = N$$

$$\text{NCON} = \text{NVAR} + \text{NMEQ}$$

The objective function is,

$$\Delta G^t = \frac{G^t - \sum_{i=1}^N n_i^o G_i^o}{RT} = \sum_{i=1}^N \sum_{p=1}^{\pi} n_{ip} \left[\ln \left(P \phi_{ip} \frac{n_{ip}}{n_{Tp}} \right) \right]$$

and the constraints are,

$$C_1 \equiv n_i^o - \sum_{p=1}^{\pi} n_{ip} = 0 \quad i = 1, \dots, N$$

$$C_2 \equiv n_i^o \geq n_{ip} \geq 0$$

The gradient of the objective function and the constraints with respect to the mole number of the i th species in the p th phase n_{ip} are,

$$\frac{\partial \Delta G^t}{\partial n_{ip}} = \ln \left(P \phi_i^p \frac{n_{ip}}{n_{Tp}} \right) + \sum_{j=1}^N n_{jp} \left[\frac{\partial \ln \phi_j^p}{\partial n_{ip}} + \frac{\partial n_{jp}}{\partial n_{ip}} \frac{1}{n_{jp}} - \frac{1}{n_{Tp}} \right]$$

and

$$\frac{\partial C_1}{\partial n_{ip}} \equiv \frac{\partial C_2}{\partial n_{ip}} \equiv 1$$

Notice, that since the derivatives of the constraints for both the chemical and physical equilibrium problems are constant, they are evaluated only once.

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About the Author



Dr. Melhem is an internationally known pressure relief and flare systems, chemical reaction systems, process safety, and risk analysis expert. In this regard he has provided consulting, design services, expert testimony, incident investigation, and incident reconstruction for a large number of clients. Since 1988, he has conducted and participated in numerous studies focused on the risks associated with process industries fixed facilities, facility siting, business interruption, and transportation.

Prior to founding ioMosaic Corporation, Dr. Melhem was president of Pyxsys Corporation; a technology subsidiary of Arthur D. Little Inc. Prior to Pyxsys and during his twelve years tenure at Arthur D. Little, Dr. Melhem was a vice president of Arthur D. Little and managing director of its Global Safety and Risk Management Practice and Process Safety and Reaction Engineering Laboratories.

Dr. Melhem holds a Ph.D. and an M.S. in Chemical Engineering, as well as a B.S. in Chemical Engineering with a minor in Industrial Engineering, all from Northeastern University. In addition, he has completed executive training in the areas of Finance and Strategic Sales Management at the Harvard Business School. Dr. Melhem is a Fellow of the American Institute of Chemical Engineers (AIChE) and Vice Chair of the AIChE Design Institute for Emergency Relief Systems (DiERS).

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Index

Dust, 16

Flammability, 16

ioKinetic, 16

ioMosaic, 16

ISO, 16



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