Validated Computing Approach for High-Pressure Chemical and Multiphase Equilibrium

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Abstract

For the computation of chemical and phase equilibrium at constant temperature and pressure, there have been proposed a wide variety of problem formulations and numerical solution procedures, involving both direct minimization of the Gibbs energy and the solution of equivalent nonlinear equation systems. Still, with very few exceptions, these methodologies may fail to solve the chemical and phase equilibrium problem correctly. Nevertheless, there are many existing solution methods that are extremely reliable in general and fail only occasionally. To take good advantage of this wealth of available techniques, we demonstrate here an approach in which such techniques can be combined with procedures that have the power to *validate* results that are correct, and to identify results that are incorrect. Furthermore, in the latter case, corrective feedback can be provided until a result that can be validated as correct is found. The validation procedure is *deterministic,* and provides a mathematical and computational *guarantee* that the *global* minimum in the Gibbs energy has been found. To demonstrate this validated computing approach to the chemical and phase equilibrium problem, we present several examples involving reactive and nonreactive components at high pressure, using cubic equation-of-state models.

1. Introduction

Knowledge of phase equilibrium, with or without simultaneous chemical reactions, is clearly important in the design and analysis of a wide variety of chemical processing operations, including reactors and separation units. Even in the case of kinetically-limited reactions, knowledge of chemical and phase equilibrium can offer insight into the behavior of a system by pointing out thermodynamic limitations on expected conversions. We will concentrate here primarily on the case in which the operation is at high pressure and there are reactive components.

In computing chemical and phase equilibrium the basic goals are to correctly determine the number and type of phases present and the distribution of components amongst the phases at the equilibrium state. For the case of fixed temperature and pressure, which will be the focus here, the fundamental condition that must be achieved is the *global* minimization of the Gibbs energy. Though easily stated in principle, in practice the computation of chemical and phase equilibrium is a very challenging problem. As a result, there is a very large and still growing body of literature devoted to the solution of this problem. As reviewed by Seider and Widagdo [1], there have been proposed a wide variety of problem formulations and numerical solution procedures, involving both direct optimization and the solution of equivalent nonlinear equation systems. Still, with very few exceptions, as noted below, these methodologies may fail to solve the chemical and phase equilibrium problem correctly. We demonstrate here an approach in which existing solution methodologies, some of which are very reliable in general and fail only occasionally, can be combined with techniques that have the power to *validate* results that are correct, and to identify results that are incorrect. Furthermore, in the latter case, corrective feedback can be provided until a result that can be validated as correct is found.

In general, in order to provide a completely reliable method for computing chemical and phase equilibrium it is necessary to apply some form of *deterministic* global optimization procedure. Such procedures can be applied directly to the minimization of the Gibbs energy, but are more commonly applied indirectly during phase stability analysis. For example, McDonald and Floudas [2–4] apply a deterministic global optimization procedure for stability analysis when chemical and phase equilibrium is computed from various excess Gibbs energy models, and Harding and Floudas [5] do likewise for the case in which cubic equation of state models are used. In this work [2-5], the α-BB approach [6,7], which is based on a branch-and-bound strategy with convex underestimating functions, is used. An alternative deterministic procedure for phase stability analysis is the use of an interval-Newton/general-bisection (IN/GB) approach [8]. This has been demonstrated for the case of excess Gibbs energy models by Stadtherr et al. [9], McKinnon et al. [10], and Tessier et al. [11], and for the case of cubic equations of state by Hua et al. [12–14]. Recently Xu et al. [15] applied this approach to the case in which the Gibbs energy is determined using a statistical associating fluid theory (SAFT) model. Both the α-BB and IN/GB procedures are deterministic and thus provide a mathematical *guarantee* that the phase stability problem is correctly solved. The IN/GB procedure, since it uses interval arithmetic throughout, also provides a rigorous computational guarantee of global optimality [16].

To demonstrate the IN/GB procedure for phase stability analysis using cubic equation of state models, Hua [17] developed a package called INTFLASH for computing phase equilibrium. Likewise, for the case of excess Gibbs energy models, McDonald and Floudas [18] demonstrated the α-BB procedure for phase stability analysis by developing a package for chemical and phase equilibrium called GLOPEQ. However, efforts such as these do not take good advantage of the wealth of already available software for computing chemical and phase equilibrium. There are many good routines available that provide no guarantee of reliability, since they do not employ a deterministic global optimization approach, but which are nevertheless often extremely reliable. What is needed is a way to validate the results of such routines when they are correct, and to provide feedback in the occasional case for which the results are incorrect. We demonstrate here a strategy for doing this, based on the use of the IN/GB approach for phase stability analysis. In particular, we adopt a version [19] of the code CHASEOS for computing chemical and phase equilibrium from cubic equation-of-state models (a version of this code is also available as an "in house" part of the IVC-SEP package [20]). CHASEOS implements the algorithm of Castier et al. [21], an extension of the techniques of Michelsen [22,23] and Myers and Myers [24]. We show how its results can be validated, with corrective feedback as needed, using the phase stability algorithm of Hua et al. [14].

2. Methodology

Consider the problem of computing chemical and multiphase equilibrium at constant temperature and pressure in a system of NC components. This problem can be stated fundamentally as one of seeking the global minimum of the total Gibbs energy function

$$G = \sum_{i=1}^{NC} \sum_{j=1}^{NP} N_i^{(j)} \mu_i^{(j)} \tag{1}$$

with respect to the number of phases NP and the mole numbers $N_i^{(j)}$. Here $N_i^{(j)}$ indicates the number of moles of component i in phase j, and $\mu_i^{(j)}$ is the chemical potential of component i in phase j, which depends on the composition of phase j and on the given temperature T and pressure P. The mole numbers are constrained by the atom balances

$$\mathrm{A} \cdot \mathbf{N} = \mathbf{b} \tag{2}$$

and nonnegativity constraints

$$N_i^{(j)} \geq 0, \quad i = 1, \ldots, NC, \quad j = 1, \ldots, NP\,. \tag{3}$$

Here the elements A_{ki} of the matrix A indicate the number of atoms of element k in a molecule of component i, the elements $N_i = \sum_{j=1}^{NP} N_i^{(j)}$ of the vector **N** indicate the total number of moles of component i, and the elements b_k of the vector **b** indicate the given total abundance of element k in the system. Nonreactive (inert) species can be handled by treating them as "elements" when constructing the matrix A.

Solution of the problem in the above form would require the use of constrained optimization techniques. Alternatively, the problem can be reformulated in various ways to permit the use of unconstrained methods. Castier et al. [21] follow the stoichiometric formulation approach. Here a set of $NR = NC - \mathrm{rank(A)}$ independent chemical reactions is first determined, and then the mole numbers are expressed in terms of the yield factors

$$\theta_i^{(j)} = \frac{N_i^{(j)}}{N_i}, \quad i = 1, \ldots, NC, \quad j = 1, \ldots, NP\,, \tag{4}$$

and the extents of reaction ξ_k, defined by

$$N_i = N_{i,0} + \sum_{k=1}^{NR} \nu_{ik} \xi_k\,, \quad i = 1, \ldots, NC\,, \tag{5}$$

with ν_{ik} indicating the stoichiometric coefficient of component *i* in reaction *k*, and $N_{i,0}$ the initial mole number of component *i*. Note that not all of the yield factors are independent, as they are related by

$$\sum_{j=1}^{NP} \theta_i^{(j)} = 1, \quad i = 1, \ldots, NC \ . \tag{6}$$

Thus, in this problem formulation, the independent variables are the *NR* extents of reaction and the $NC(NP-1)$ independent yield factors. In Castier et al.'s algorithm [21], a local minimum of *G* is sought using the second-order unconstrained minimization algorithm of Murray [25]. To initialize the minimization procedure, ideas are adapted from Myers and Myers's work [24] on the chemical equilibrium problem and Michelsen's work [23] on the phase equilibrium problem.

Once a local minimum in *G* has been located, it is then tested for global optimality in Castier et al.'s algorithm [21] by using Michelsen's technique [22] for implementing the phase stability test given by Baker et al. [26]. This test is based on tangent plane analysis. Assume that the system to be tested has a phase with composition (mole fraction) vector **z**. Then consider the molar Gibbs energy vs. composition (mole fraction) surface $g(\mathbf{x})$ and a hyperplane tangent to $g(\mathbf{x})$ at $\mathbf{x} = \mathbf{z}$. If this tangent plane ever crosses (goes above) the Gibbs energy surface, then the system being tested is not stable (i.e., it is either unstable or metastable). This condition is often stated in terms of the tangent plane distance function

$$D(\mathbf{x}) = g(\mathbf{x}) - g_0 - \sum_{i=1}^{NC} \left(\frac{\partial g}{\partial x_i} \right)_0 (x_i - z_i) \tag{7}$$

that gives the distance of the Gibbs energy surface above the tangent plane (the subscript zero indicates evaluation at $\mathbf{x} = \mathbf{z}$). If $D(\mathbf{x})$ is negative for any value of **x**, then the system being tested is not stable. To determine if *D* is ever negative, its minimum is sought. If a stationary point (local minimum) of D is found for which $D < 0$, then this indicates that the system being tested is not stable. The composition corresponding to this stationary point is also useful to provide an initial composition estimate for a possible new equilibrium phase. Note that if a multiphase equilibrium is to be tested, then it is actually necessary to use only one of the phases in the stability test, since they share the same tangent plane at the equilibrium compositions to be tested. In Castier et al.'s algorithm [21], if it is found that the equilibrium determined from the local minimization is not stable (not globally optimal), then a new phase is added, and the composition at the stationary point yielding a negative *D* is used to reinitialize before performing another local minimization of *G*. The minimization of *G* includes provisions for possible removal of a phase. Complete details of this algorithm for computing chemical and phase equilibrium are given by Castier et al [21].

While the algorithm outlined above is very reliable, it can fail if the *global* minimum in *D* is not found during phase stability analysis. If the global minimum in *D* is negative, but is missed during the phase stability analysis, this can result in a situation in which the algorithm returns a result that is not a stable equilibrium state. It is this difficulty that motivated the work referred to above on the use of deterministic global optimization in doing phase stability analysis.

Because the results of Castier et al.'s [21] code CHASEOS (or any other code for chemical and phase equilibrium not based on deterministic global optimization) may not be correct, there is a need for a validation procedure. For this, we apply here the technique of Hua et al. [14] for performing phase stability analysis. This is a *deterministic* technique that provides a mathematical and computational *guarantee* that the *global* minimum in the tangent plane distance function *D* is found. The method is based on interval mathematics, in particular an interval-Newton approach combined with generalized bisection (IN/GB).

For general background on interval mathematics, including interval-Newton methods, there are several good sources [16,27,28]. Details of the particular IN/GB algorithm employed here are given by Schnepper and Stadtherr [8] and Hua et al. [14]. An important feature of this approach is that, unlike standard methods for nonlinear equation solving and/or optimization that require a *point* initialization, the IN/GB methodology requires only an initial *interval*, and this interval can be sufficiently large to enclose all feasible results. Thus, in the case of phase stability analysis, all composition variables (mole fractions) can be initialized to the interval [0,1]. Intervals are searched for stationary points using a powerful root inclusion test based on the interval-Newton method. This test can determine with mathematical certainty if an interval contains no stationary point or if it contains a *unique* stationary point. If neither of these results can be proven, then typically the interval is bisected and the root inclusion test applied to each subinterval. On completion, the IN/GB algorithm will have determined narrow enclosures of *all* the stationary points of *D*, and the global minimum can be readily determined. Alternatively, IN/GB can be applied in connection with a branch-and-bound scheme, which will lead directly to the global minimum without finding any of the other stationary points. This IN/GB approach for phase stability was implemented by Hua et al. [14] in the code referred to here as INTSTAB.

When the code CHASEOS implementing Castier et al.’s algorithm [21] returns a result, the composition of one of the phases (or of the only phase if it is a single phase result) is passed to INTSTAB for validation using phase stability analysis. If INTSTAB determines that the system is stable, then this validates that the result found by CHASEOS is indeed correct. If INTSTAB determines that the system is not stable, then this indicates that the results returned by CHASEOS are incorrect. In this case, the stationary point corresponding to the global minimum in *D* will have a negative value of *D*. The composition at this stationary point is then returned to CHASEOS, where a new phase is added and the composition at the stationary point used to reinitialize before performing another local minimization of *G*. This process appears to the CHASEOS code just as if it were a stationary point with negative *D* value found by its own stability analysis routine. Castier et al.'s algorithm [21] is then executed until a new result is returned for validation by INTSTAB. This type of two-stage strategy in which phase split computations (local minimization of *G*) alternates with phase stability analysis (global optimality check on local minimum of *G*) can be shown (e.g., [10]) to converge in a finite number of steps to the equilibrium state (global minimum of *G*) provided that a deterministic procedure is used to globally minimize the tangent plane distance function in doing phase stability tests. In fact, CHASEOS already uses such a two-stage strategy [22,23] internally, but the procedure used to test phase stability is not deterministic and may fail to give the correct result.

What we have described here is the integration of Hua et al.'s [14] INTSTAB with Castier et al.'s [21] CHASEOS to provide validation of the results from CHASEOS, as well as corrective feedback if needed. This validated computing approach could be used in connection with many other codes for chemical and phase equilibrium as well. If validation alone is desired, then the chemical and phase equilibrium code can be treated simply as a black box. If corrective feedback is also desired, then access to the source code is required, so that feedback can be inserted at the proper point in the code.

3. Results and Discussion

We test here the validated version of CHASEOS, which we will refer to as V-CHASEOS, for several cases involving chemical and phase equilibrium at high pressure. In these examples, cubic equation-of-state (EOS) models, either Soave-Redlich-Kwong (SRK) or Peng-Robinson (PR), are used with standard van der Waals mixing rules incorporating a single binary interaction parameter k_{ij} per component pair. Since the original CHASEOS code is in our experience quite reliable, our anticipation is that in most cases, V-CHASEOS will serve simply to validate the results from CHASEOS, and that no corrective feedback will be needed.

3.1 Problem 1: Methanol Synthesis

This system has five reactive components, CO, CO_2, H_2, H_2O and CH_3OH, and one inert, CH_4. It is a system that has been studied previously by various authors [21,29–32]. There are two independent reactions:

$$\mathrm{CO} + 2\mathrm{H}_2 \leftrightarrow \mathrm{CH}_3\mathrm{OH}$$
$$\mathrm{CO}_2 + \mathrm{H}_2 \leftrightarrow \mathrm{CO} + \mathrm{H}_2\mathrm{O}\,.$$

This reactive system was modeled at 473.15 K and 300 atm, using the SRK EOS model to be consistent with the work of Jalali-Frahani and Seader [31,32]. Formation data (ΔG and ΔH), heat capacity data, and critical properties for each component were obtained from Reid et al. [33] and the k_{ij} used are the same as those used by Jalali-Frahani and Seader [31]. The feed consists of 15 moles of CO, 8 moles of CO_2, 74 moles of H_2, and 3 moles of CH_4, values also taken from [31].

Table 1 shows the results of applying V-CHASEOS to this problem. The first part of the table shows the composition (mole fractions), total amount (moles) and molar volume (cm^3/mole) of each phase as determined by CHASEOS. The second part of the table shows the stationary points found in the phase stability analysis when using INTSTAB to validate these equilibrium phase results. Since none of the stationary points has a negative value of the tangent plane distance D, the solution returned by CHASEOS has been validated as the correct solution. This is consistent with the solution reported in [31]. Although this result can be found using Castier et al.'s algorithm [21] as implemented in CHASEOS, as well as by various other methods for computing chemical and phase equilibrium, such as the continuation-based approach of Jalali-Frahani and Seader [31,32], by using the validated computing approach implemented here in V-CHASEOS we obtain the added value of a mathematical and computational *guarantee* that the correct results have in fact been obtained. Of course, this guarantee comes at an additional computational expense. For this six-component problem, the additional CPU time required by INTSTAB to do the validation was about 32 seconds, on a Sun Blade 1000 Model 1600 (600 MHz) workstation (all other timing results reported below are for the same machine).

3.2 Problem 2: Cyclohexane Synthesis

The calculation of chemical and phase equilibrium in the hydrogenation of benzene to produce cyclohexane was originally studied by George et al. [34] and later, by Castillo and Grossman [35]. This system has three reactive components, C_6H_6, H_2, and C_6H_6, one independent reaction

$$\mathrm{C_6H_6} + 3\mathrm{H_2} \leftrightarrow \mathrm{C_6H_{12}},$$

and is at 500 K and 30 atm. George et al. [34] and Castillo and Grossman [35] used the Lewis fugacity model for this system. V-CHASEOS is based on cubic EOS models, so we used the PR EOS model. Formation data and critical properties were taken from the

ASPEN PLUS® database, heat capacity data from Reid et al. [33], and all k_{ij} values were set to zero. The feed [34,35] consists of 1 mole of benzene and 3.05 moles of hydrogen.

The results of applying V-CHASEOS to this problem are shown in Table 2. Again the first part of the table shows the equilibrium phase results returned by CHASEOS, and the second part shows the stationary points determined by INTSTAB in the validation step. Since none of these stationary points has a negative value of D, the result returned originally by CHASEOS is again validated to be correct. The CPU time required by INTSTAB for the validation was about 0.12 seconds.

The chemical and phase equilibrium results determined and validated here do not match those reported by George et al. [34] and Castillo and Grossman [35]. This could be because they used a different model, or because they found a local, but not global, minimum of G in their calculations. Because their reported results include a phase with composition very similar to that of the third stationary point given in Table 2, we initially suspected the latter explanation. To determine the true explanation, we applied the IN/GB method to solve the nonlinear equation system corresponding to the equifugacity conditions for the Lewis model, with model parameters taken from George et al. [34]. This allowed us to find with certainty *all* solutions to the equifugacity condition, and to then validate that in fact the solution reported by George et al. [34] and Castillo and Grossman [35] was the global minimum in G when the Lewis fugacity model is used. Thus the difference in the reported solutions is due simply to the difference in choice of models. Since the IN/GB approach was used to validate the results obtained from both models, it is possible to draw this conclusion with complete certainty. In comparing different models for representing equilibrium behavior, and deciding how well they fit experimental data, it is important that computed model results be validated. Otherwise it is possible that a model could be considered inadequate, when in fact the difficulty is that an incorrect equilibrium solution was computed from the model.

3.3. Problem 3: Esterification in Supercritical CO_2

The esterification of acetic acid with ethanol to form ethyl acetate and water in supercritical CO_2 was studied experimentally by Blanchard and Brennecke [36] at 60ºC and 57.8 atm. This indicated that the use of supercritical CO_2 enhanced the conversion to ethyl acetate to 72%, as compared to the neat liquid reaction, which only proceeds to 63% conversion. Two equilibrium phases were observed during this experimental study. We attempt to model this system here using the PR EOS.

The system has four reactive components, acetic acid, ethanol, ethyl acetate, and water, and it is assumed that CO_2 is inert, since there was no evident change in the amount of CO_2 during the course of the experiments. There is one independent reaction

$$\mathrm{C_2H_4O_2 + C_2H_5OH \leftrightarrow C_4H_8O_2 + H_2O}\ ,$$

and the feed consists of 3.64 moles of ethanol, 3.64 moles of acetic acid, and 2.72 moles of CO_2. Computational results for three different models are presented here. For all models, formation data, heat capacity data, and critical properties were obtained from Reid et al. [33]. For Model I, k_{ij} values were regressed from binary VLE data using Aspen PLUS®. These values, as well as references for the VLE data used, are given in Table 3.

Table 4 shows the results of applying V-CHASEOS to compute the chemical and phase equilibrium for Model I. Shown first in the table is the result returned initially from CHASEOS, which indicates a single phase at equilibrium. Shown next are the stationary points returned by INTSTAB to validate the single-phase equilibrium solution. It is observed that the single-phase solution is validated to be stable.

Since Blanchard and Brennecke [36] observed two equilibrium phases experimentally, not just one, a brief, nonsystematic, and ultimately not very successful effort was made to adjust some of the k_{ij} values to better model the experimental results. In doing so, Models II and III were encountered. Both are interesting from a computational standpoint, though neither accurately models the experimental observations. The k_{ij} values for these two models are also listed in Table 3.

The results of applying V-CHASEOS to compute the chemical and phase equilibrium for Model II are shown in Table 5. Shown first are the results returned from CHASEOS, which indicates a single equilibrium phase. Shown next are the stationary points returned by INTSTAB. Since there are stationary points corresponding to negative values of the tangent plane distance D, this indicates that the single-phase solution returned by CHASEOS is incorrect, and that corrective feedback is necessary. The stationary point with the lowest (most negative) value of D is chosen (stationary point IV), and these composition values are returned to CHASEOS as described above for addition of a new phase and reinitialization of Gibbs energy minimization. The result now returned by CHASEOS is shown next in the table, and indicates a two-phase equilibrium. Finally, the stationary points found by INTSTAB in testing this two-phase solution are shown, indicating, since none has negative value of D, that this is the validated equilibrium solution for this problem. The computing time required for the validation on this problem was unusually large, about 2950 CPU seconds for the initial use of INTSTAB to identify the incorrect solution, and about 3120 CPU seconds for the final validation of the correct answer. Of course, this additional computation time was well spent, since, without the validation, the prediction of Model II would have been reported erroneously as single phase, when in fact the model predicts that there are two phases.

Table 6 shows the results of applying V-CHASEOS to Model III. Here the initial result from CHASEOS shows a two-phase equilibrium. Next, it is seen that INTSTAB identifies stationary points with negative values of *D*, indicating that this result from CHASEOS was incorrect. Corrective feedback is now provided to CHASEOS, and it next returns a different two-phase result, as shown in the table. Application of INTSTAB to this result again leads to a stationary point with negative *D* and so CHASEOS has still not found the correct equilibrium result. Corrective feedback to CHASEOS is once again provided, and this time it returns a three-phase result, which INTSTAB validates as correct, since all the stationary points in this second repeat application of INTSTAB are nonnegative, as shown in the table. Again, this is a case in which, for a particular model, the correct equilibrium result is not found by CHASEOS, but is found by V-CHASEOS by the use of validation and corrective feedback.

For none of the models used above do the computed and validated predictions of the PR EOS model closely match the equilibrium measurements of Blanchard and Brennecke [36]. This is most likely due to the inadequacies of the PR EOS in modeling systems, such as this one, for which there is a high degree of association due to hydrogen bonding. Some improvements in the prediction could be likely achieved by a less cursory and more systematic effort in adjusting the values of the k_{ij}, but use of a different model may be more appropriate.

3.4 Problem 4: Methane – Carbon dioxide – *n*-Hexane – Hydrogen

This system involves four components, methane, CO_2, *n*-hexane, and hydrogen, and is taken from work by Zhu et al. [37]. They implemented a *stochastic* global optimization approach for phase stability analysis, based on a simulated annealing algorithm. While this approach offers no guarantee that the phase stability analysis will be done correctly, and thus is not appropriate for use in the context of validation, it should nevertheless be very reliable. Their simulated annealing approach was developed for the case of nonreactive systems, but can be readily applied to reactive systems as well. Zhu et al. [37] claim that the interval approach used by Hua et al. [14] in INTSTAB leads to uncertainties because "it cannot be certain that within an interval there exist one or multiple solutions." This statement is incorrect, and in fact just the opposite is true. The interval-Newton method [16,27,28] used by Hua et al. [14] provides a powerful existence and uniqueness test for solutions in an interval, and even in pathological cases (solution at a singular point) for which interval-Newton is inconclusive (though still guaranteed to enclose all solutions), there are techniques [38] now available for determining the existence of a solution in an interval.

As reported by Zhu et al. [37], this system was modeled using the SRK EOS at 200 K and 42.5 bar, and with a feed consisting of 0.5 moles of methane, 0.0574 moles of CO_2, 0.0263 moles of *n*-hexane, and 0.4163 moles of hydrogen. We used physical property data and binary interaction parameters taken from the ASPEN PLUS® database. Two variations of this problem are considered here, the case in which the components are nonreactive, and the hypothetical case in which they are reactive.

For the hypothetical reactive case, the independent reaction identified by CHASEOS is

$$6\mathrm{CH}_4 \leftrightarrow \mathrm{C}_6\mathrm{H}_{14} + 5\mathrm{H}_2 .$$

The results of applying V-CHASEOS for this case are shown in Table 7, which indicates a validated, single-phase equilibrium solution. The CPU time required for the validation step was about 5.8 seconds.

For the nonreactive case, hydrogen is specified to be inert, leading to a phase equilibrium calculation only, the case considered in Zhu et al. [37]. Table 8 shows the results of applying V-CHASEOS for this case. Here there is a validated, two-phase equilibrium solution (validation time was about 41 CPU seconds). However, these results disagree substantially with those given by Zhu et al. [37]. The phase equilibrium results from Zhu et al. [37] were then tested using INTSTAB and found to not represent a stable system. After some additional study, we eventually reached the conclusion, that, despite repeatedly identifying the fourth component in this system as hydrogen, Zhu et al. [37] were apparently using hydrogen *sulfide* as the fourth component. Thus, as a final example, we consider the system of methane, CO_2, *n*-hexane, and hydrogen sulfide.

3.5 Problem 5: Methane – Carbon Dioxide – *n*-Hexane – Hydrogen Sulfide

This problem is the same as considered in the previous example, except that the fourth component is hydrogen sulfide, not hydrogen. The system is treated as nonreactive, and the feed composition, temperature and pressure are as given above. This problem has been studied by Kohse and Heidemann [39], Sun and Seider [40] and (apparently) Zhu et al. [37]. It is a challenging problem, since at this temperature and pressure the feed composition puts this mixture near a tricritical point [39]. Zhu et al. [37] claim that the two-phase equilibrium result computed by Sun and Seider [40] is just a local minimum in the Gibbs energy. However, as discussed below, it is not clear that this claim is actually true.

The binary interaction parameter values used by Sun and Seider [40] are known [41], and are listed in Table 9 as Model A (this accounts for correction of a typographical error in [41] in which two component indices are inadvertently switched). However, the exact physical property data used by Sun and Seider [40] are not known, and so we have used the average of the values found in Reid et al. [33] and in the ASPEN PLUS® database. These physical property values are listed in Table 10 as Model A.

Using this data for Model A, V-CHASEOS was applied to compute and validate the phase equilibrium for this system. The results are shown in Table 11. The first part of the table shows that CHASEOS returns a two-phase equilibrium solution, which is similar to (though not exactly the same as) the result reported by Sun and Seider [40]. The second part of the table shows that, when INTSTAB is applied to validate this equilibrium solution, there are three stationary points found, and that all have a nonnegative value of D. Thus, this two-phase result is validated, and represents a global minimum in the Gibbs energy. This leads us to believe that the result given by Sun and Seider [40] is a most likely a correct two-phase equilibrium, contrary to the claim by Zhu et al. [37]. However, it should be emphasized that we cannot say this with certainty, since we do not know the exact physical property data used by Sun and Seider [40], and for this problem the predicted phase equilibrium is very sensitive to the model parameter values, as seen below. The CPU time required by INTSTAB for validation in this problem was about 120 seconds.

Zhu et al. [37] compute a 3-phase equilibrium for this problem. However, they took binary interaction parameter values from the program MULPRG, which is attributed without citation to Michelsen. To try to replicate the model used by Zhu et al. [37], we thus took k_{ij} values, as well as physical property data, from Michelsen's LNGFLASH code, part of the IVC-SEP package [20]. These values are given in Tables 9 and 10 as Model B. With these new values of the binary interaction parameters and physical property data, V-CHASEOS was run again to compute and validate the phase equilibrium, with the results given in Table 12. This shows a validated three-phase solution, with compositions that are very close to those given by Zhu et al. [37], though not quite identical. We assume that this difference is due to slight differences in the model parameters used, since the computed equilibrium result (*including number of phases*) is clearly very sensitive to small changes in the model parameters (k_{ij} and pure component physical property data) in this region of complex phase behavior. The CPU time required by INTSTAB for validation in this case was about 109 seconds.

In summary, we believe it likely that both Sun and Seider [40] and Zhu et al. [37] computed correct equilibrium solutions that globally minimize the Gibbs energy. Their solutions differ in the number of phases because they used slightly different model parameters. The conclusion that the two-phase result for Model A and the three-phase result for Model B are both correct can be made with certainty because of the validation procedure used in V-CHASEOS. Without such validation, it would be tempting to conclude, since the model parameters are nearly the same, that one of the solutions is incorrect.

4. Concluding Remarks

The computation of chemical and phase equilibrium is a very challenging problem. There have been proposed a wide variety of problem formulations and numerical solution procedures, involving both direct optimization and the solution of equivalent nonlinear equation systems. Still, with very few exceptions, as noted above, these methodologies may fail to solve the chemical and phase equilibrium problem correctly. Nevertheless, there are many existing solution methods that are extremely reliable in general and fail only occasionally. To take good advantage of this wealth of available techniques, we have demonstrated here an approach in which such techniques can be combined with procedures, based on interval analysis, that have the power to *validate* results that are correct, and to identify results that are incorrect. Furthermore, in the latter case, corrective feedback can be provided until a result that can be validated as correct is found. The validation procedure is *deterministic*, and provides a mathematical and computational *guarantee* that the *global* minimum in the Gibbs energy has been found.

We have demonstrated the validation procedure here using CHASEOS, a standalone code for chemical and phase equilibrium, that implements the algorithm of Castier et al. [21], an extension of the techniques of Michelsen [22,23] and Myers and Myers [24]. However, this validated computing approach could also be used in connection with many other standalone codes for chemical and phase equilibrium. If validation alone is desired, then the chemical and phase equilibrium code can be treated simply as a black box. If corrective feedback is also desired, then access to the source code is required, so that feedback can be inserted at the proper point in the code. This approach to validated computing could also be used for chemical and phase equilibrium computations in the context of a process simulator. In this case, since the equilibrium computation may be nested inside some other iterative calculation, it is likely not desirable to invoke the validation procedure every time an equilibrium computation is done. Instead, the validation step should be applied only after the entire simulation is complete. The validation comes at the cost of additional computing time. Thus a modeler may need to consider the trade off between the additional computing time and the risk of getting the wrong answer to a chemical and phase equilibrium problem. Certainly, for “mission critical” situations, the additional computing expense is well spent.

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List of Symbols

A	matrix with elements A_{ki}
A_{ki}	number of atoms of element k in a molecule of component i
b	vector with elements b_k
b_k	total abundance of element k
D	tangent plane distance, Eq. (7)
g	molar Gibbs energy
G	total Gibbs energy
k_{ij}	binary interaction parameter
N	vector with elements N_i
N_i	total number of moles of component i
$N_{i,0}$	initial number of moles of component i
$N_i^{(j)}$	number of moles of component i in phase j
NC	number of components

NP	number of phases
NR	number of independent chemical reactions
P	pressure
T	temperature
$\mathbf{x}$	a composition (mole fraction) vector
$\mathbf{z}$	composition (mole fraction) vector of phase being tested in stability analysis

Greek letters

$\theta_i^{(j)}$	yield factor for component i in phase j, Eq. (4)
$\mu_i^{(j)}$	chemical potential for component i in phase j
ν_{ik}	stoichiometric coefficient of component i in reaction k
ξ_k	extent of reaction k

Subscript

0	indicates evaluation at $\mathbf{x} = \mathbf{z}$ in stability analysis

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Table 1. Results for Problem 1, using the SRK EOS at 473.15 K and 300 atm.

	Composition [mole fraction][a]						Total [moles]	V [cm^3/mol]	D
CHASEOS	CO	CO_2	H_2	H_2O	CH_3OH	CH_4			
Phase I (L)	0.105 x 10^{-4}	0.231 x 10^{-3}	0.976 x 10^{-1}	0.243	0.634	0.248 x 10^{-1}	27.759	60.09	
Phase II (V)	0.624 x 10^{-4}	0.515 x 10^{-3}	0.660	0.471 x 10^{-1}	0.204	0.879 x 10^{-1}	26.285	133.45	
INSTAB									
Stationary Point I	0.105 x 10^{-4}	0.231 x 10^{-3}	0.976 x 10^{-1}	0.243	0.634	0.248 x 10^{-1}		60.09	0.000
Stationary Point II	0.624 x 10^{-4}	0.515 x 10^{-3}	0.660	0.471 x 10^{-1}	0.204	0.879 x 10^{-1}		133.45	0.000
Stationary Point III	0.368 x 10^{-4}	0.470 x 10^{-3}	0.340	0.114	0.477	0.685 x 10^{-1}		87.67	0.041

[a] In this and other tables of results, mole fractions will not sum precisely to one due to rounding of computer output during transcription to the tables.

Table 2. Results for Problem 2, using the PR EOS at 500K and 30 atm.

	Composition [mole fraction]			Total [moles]	V [cm^3/mol]	D
CHASEOS	C_6H_6	H_2	C_6H_{12}			
Phase I (L)	0.492×10^{-5}	0.147×10^{-1}	0.985	0.902	159.82	
Phase II (V)	0.400×10^{-5}	0.249	0.751	0.148	1064.03	
INTSTAB						
Stationary Point I	0.492×10^{-5}	0.147×10^{-1}	0.985		159.82	0.000
Stationary Point II	0.400×10^{-5}	0.249	0.751		1064.03	0.000
Stationary Point III	0.460×10^{-5}	0.764×10^{-1}	0.924		375.95	0.078

Table 3. Binary interaction parameters used in Problem 3.

	Model I		Model II	Model III
Binary Pair	k_{ij}	Refs.	k_{ij}	k_{ij}
CO_2 – Ethanol	0.0917	[42]	0.0917	0.0917
CO_2 – Acetic Acid	0.0363	[43]	0.0363	0.0363
CO_2 – H_2O	-0.0923	[44, 45]	-0.0923	-0.0923
CO_2 – Ethyl Acetate	-0.1339	[46]	-0.1339	0.000
H_2O – Acetic Acid	-0.144	[47]	-0.144	-0.144
H_2O – Ethanol	-0.0935	[47]	-0.935	-0.935
H_2O – Ethyl Acetate	-0.280	[47]	-0.280	-0.280
Ethanol – Acetic Acid	-0.0436	[47]	-0.0436	-0.0436
Ethanol – Ethyl Acetate	0.022	[47]	0.022	0.022
Acetic Acid – Ethyl Acetate	-0.0226	[47]	-0.226	-0.226

Table 4. Results for Problem 3, using the PR EOS with Model I k_{ij} values, at 333.15K and 57.8 atm.

	Composition [mole fraction]					Total [moles]	V [cm^3/mol]	D
CHASEOS	C_2H_5OH	$C_2H_4O_2$	$C_4H_8O_2$	H_2O	CO_2			
Phase I (L)	0.223	0.223	0.141	0.141	0.272	10	61.28	
INTSTAB								
Stationary Point I	0.223	0.223	0.141	0.141	0.272		61.28	0.000
Stationary Point II	0.940×10^{-2}	0.240×10^{-2}	0.109×10^{-1}	0.345×10^{-2}	0.974		340.04	0.324
Stationary Point III	0.278×10^{-1}	0.124×10^{-1}	0.676×10^{-1}	0.889×10^{-2}	0.883		133.40	0.401

Table 5. Results for Problem 3, using the PR EOS with Model II k_{ij} values, at 333.15K and 57.8 atm.

	Composition [mole fraction]					Total [moles]	V [cm^3/mol]	D
CHASEOS	C_2H_5OH	$C_2H_4O_2$	$C_4H_8O_2$	H_2O	CO_2			
Phase I (L)	0.196	0.196	0.168	0.168	0.272	10	59.72	
INTSTAB								
Stationary Point I	0.196	0.196	0.168	0.168	0.272		59.72	0.000
Stationary Point II	0.229×10^{-2}	0.126×10^{-2}	0.815×10^{-2}	0.596×10^{-3}	0.988		347.51	0.063
Stationary Point III	0.860×10^{-2}	0.119×10^{-1}	0.786×10^{-1}	0.213×10^{-2}	0.899		112.90	0.181
Stationary Point IV	0.390	0.634×10^{-4}	0.658×10^{-6}	0.608	0.105×10^{-2}		36.41	-1.273
Stationary Point V	0.480×10^{-1}	0.220	0.271	0.326×10^{-1}	0.427		68.14	-0.628
CHASEOS (repeat)								
Phase I (L)	0.401	0.244×10^{-3}	0.377×10^{-5}	0.595	0.352×10^{-2}	3.527	36.88	
Phase II (L)	0.130×10^{-1}	0.232	0.331	0.642×10^{-2}	0.418	6.473	72.05	
INTSTAB (repeat)								
Stationary Point I	0.130×10^{-1}	0.23167	0.133	0.642×10^{-2}	0.418		72.05	0.000
Stationary Point II	0.401	0.244×10^{-3}	0.379×10^{-5}	0.595	0.352×10^{-2}		36.88	0.000
Stationary Point III	0.910×10^{-3}	0.137×10^{-2}	0.122×10^{-1}	0.171×10^{-3}	0.985		344.81	0.213
Stationary Point IV	0.285×10^{-2}	0.997×10^{-2}	0.876×10^{-1}	0.497×10^{-3}	0.899		125.97	0.307
Stationary Point V	0.303	0.132	0.811×10^{-1}	0.285	0.199		51.02	0.625

Table 6. Results for Problem 3, using the PR EOS with Model III k_{ij} values, at 333.15K and 57.8 atm.

	Composition [mole fraction]					Total [moles]	V [cm^3/mol]	D
CHASEOS	C_2H_5OH	$C_2H_4O_2$	$C_4H_8O_2$	H_2O	CO_2			
Phase I (L)	0.213	0.213	0.169	0.170	0.235	9.510	60.76	
Phase II(V)	0.223×10^{-2}	0.123×10^{-2}	0.746×10^{-2}	0.471×10^{-3}	0.989	0.490	349.45	
INTSTAB								
Stationary Point I	0.213	0.213	0.169	0.170	0.235		60.76	0.000
Stationary Point II	0.223×10^{-2}	0.123×10^{-2}	0.746×10^{-2}	0.471×10^{-3}	0.989		349.45	0.000
Stationary Point III	0.129×10^{-1}	0.224×10^{-1}	0.845×10^{-1}	0.269×10^{-2}	0.877		94.43	0.161
Stationary Point IV	0.398	0.784×10^{-4}	0.103×10^{-5}	0.601	0.127		36.70	-1.185
Stationary Point V	0.601×10^{-1}	0.274	0.290	0.349×10^{-1}	0.341		71.06	-0.061
CHASEOS (repeat 1)								
Phase I (L)	0.409	0.250×10^{-3}	0.506×10^{-5}	0.586	0.473×10^{-2}	3.506	37.22	
Phase II(L)	0.171×10^{-1}	0.238	0.322	0.624×10^{-2}	0.416	6.494	72.34	
INTSTAB (repeat 1)								
Stationary Point I	0.409	0.250×10^{-3}	0.506×10^{-5}	0.586	0.473×10^{-2}		37.22	0.000
Stationary Point II	0.171×10^{-1}	0.238	0.322	0.624×10^{-2}	0.416		72.34	0.000
Stationary Point III	0.819×10^{-3}	0.972×10^{-3}	0.834×10^{-2}	0.122×10^{-3}	0.990		349.78	-0.017
Stationary Point IV	0.487×10^{-2}	0.199×10^{-1}	0.979×10^{-1}	0.713×10^{-3}	0.877		92.42	0.147
Stationary Point V	0.309	0.120	0.724×10^{-1}	0.272	0.227		50.45	0.581

(continued on next page)

Table 6 (continued)

CHASEOS (repeat 2)								
Phase I (L)	0.410	0.253 x 10^{-3}	0.520 x 10^{-5}	0.585	0.466 x 10^{-2}	3.507	37.24	
Phase II(L)	0.173 x 10^{-1}	0.243	0.329	0.632 x 10^{-2}	0.405	6.362	72.80	
Phase II (V)	0.842 x 10^{-3}	0.996 x 10^{-3}	0.868 x 10^{-2}	0.123 x 10^{-3}	0.989	0.131	349.53	
INTSTAB (repeat 2)								
Stationary Point I	0.410	0.253 x 10^{-3}	0.520 x 10^{-5}	0.585	0.466 x 10^{-2}		37.24	0.000
Stationary Point II	0.173 x 10^{-1}	0.243	0.329	0.632 x 10^{-2}	0.405		72.80	0.000
Stationary Point III	0.842 x 10^{-3}	0.996 x 10^{-3}	0.868 x 10^{-2}	0.123 x 10^{-3}	0.989		349.53	0.000
Stationary Point IV	0.484 x 10^{-2}	0.193 x 10^{-1}	0.978 x 10^{-1}	0.694 x 10^{-3}	0.877		94.05	0.161
Stationary Point V	0.310	0.121	0.739 x 10^{-1}	0.272	0.223		50.62	0.582

Table 7. Results for the hypothetical reactive system in Problem 4, using the SRK EOS at 200K and 42.5 bar.

	Composition [mole fraction]				Total [moles]	V [cm^3/mol]	D
CHASEOS	CH_4	CO_2	C_6H_{14}	H_2			
Phase I (V)	0.658	0.574×10^{-1}	0.398×10^{-30}	0.285	1.0	314.88	
INTSTAB							
Stationary Point I	0.658	0.574×10^{-1}	0.398×10^{-30}	0.285		314.88	0.000

Table 8. Results for the nonreactive system in Problem 4, using the SRK EOS at 200K and 42.5 bar.

	Composition [mole fraction]				Total [moles]	V [cm^3/mol]	D
CHASEOS	CH_4	CO_2	C_6H_{14}	H_2			
Phase I (L)	0.249	0.194	0.542	0.153×10^{-1}	0.484×10^{-1}	82.14	
Phase II (V)	0.513	0.505×10^{-1}	0.295×10^{-4}	0.437	0.952	341.10	
INTSTAB							
Stationary Point I	0.249	0.194	0.542	0.153×10^{-1}		82.14	0.000
Stationary Point II	0.513	0.505×10^{-1}	0.295×10^{-4}	0.437		341.10	0.000
Stationary Point III	0.654	0.204	0.254×10^{-1}	0.116		67.36	0.348

Table 9. Binary interaction parameters used in Problem 5.

	Model A	Model B
Binary Pair	k_{ij}	k_{ij}
Methane – CO_2	0.093	0.12
Methane – *n*-Hexane	0.036	0.0
Methane – H_2S	0.08	0.08
CO_2 – *n*-Hexane	0.118	0.15
CO_2 – H_2S	0.099	0.12
n-Hexane – H_2S	0.05	0.06

Table 10. Pure component physical property data used in problem 5.

	Model A			Model B		
Component	T_c [K]	P_c [atm]	ω	T_c [K]	P_c [atm]	ω
CH_4	190.515	45.482	0.0105	190.6	45.4	0.008
CO_2	304.125	72.815	0.235	304.2	72.8	0.225
n-C_6H_{14}	507.400	29.706	0.300	507.4	29.3	0.296
H_2S	373.375	88.562	0.0905	373.2	88.2	0.1

Table 11. Results for Problem 5, using the SRK EOS at 200K and 42.5 bar, with Model A parameter values.

	Composition [mole fraction]				Total [moles]	*V* [cm^3/mole]	*D*
CHASEOS	CH_4	CO_2	C_6H_{14}	H_2S			
Phase I (L)	0.328	0.720×10^{-1}	0.363×10^{-1}	0.564	0.724	38.94	
Phase II (V)	0.952	0.189×10^{-1}	0.256×10^{-4}	0.289×10^{-1}	0.276	228.83	
INTSTAB							
Stationary Point I	0.328	0.720×10^{-1}	0.363×10^{-1}	0.564		38.94	0.000
Stationary Point II	0.952	0.189×10^{-1}	0.256×10^{-4}	0.289×10^{-1}		228.83	0.000
Stationary Point III	0.893	0.335×10^{-1}	0.144×10^{-2}	0.717×10^{-1}		79.57	0.038

Table 12. Results for Problem 5, using the SRK EOS at 200K and 42.5 bar, with Model B parameter values.

	Composition [mole fraction]				Total [moles]	V [cm^3/mol]	D
CHASEOS	CH_4	CO_2	C_6H_{14}	H_2S			
Phase I (L)	0.524	0.696×10^{-1}	0.499×10^{-1}	0.356	0.474	43.51	
Phase II (L)	0.184	0.611×10^{-1}	0.813×10^{-2}	0.747	0.324	34.69	
Phase III (V)	0.949	0.228×10^{-1}	0.267×10^{-4}	0.283×10^{-1}	0.202	227.76	
INTSTAB							
Stationary Point I	0.524	0.696×10^{-1}	0.499×10^{-1}	0.356		43.51	0.000
Stationary Point II	0.184	0.611×10^{-1}	0.813×10^{-2}	0.747		34.69	0.000
Stationary Point III	0.949	0.228×10^{-1}	0.267×10^{-4}	0.283×10^{-1}		227.76	0.000
Stationary Point IV	0.892	0.372×10^{-1}	0.166×10^{-2}	0.688×10^{-1}		81.35	0.037
Stationary Point V	0.333	0.716×10^{-1}	0.290×10^{-1}	0.567		38.46	0.003