Bilevel Optimization for Parameter Estimation in Thermodynamics
Bilevel-Optimierung zur Schätzung thermodynamischer Parameter

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades einer Doktorin der Ingenieurwissenschaften genehmigte Dissertation

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Disclaimer

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In particular, this thesis includes the parameter estimations in Aspen Data Regression System (DRS) [8] and Bilevel Optimization Algorithm for Rigorous and Robust Parameter Estimation in Thermodynamics (BOARPET) [109], the statistical and thermodynamic analysis, the formal proof and the measurement data from [59] (see item 1). These are also briefly summarized in [6]. From [88], only the measurement data and the parameter estimation are included (see item 5), while [62] is fully adopted in this thesis (see item 2). Similarly, from [61], the analysis of convexity properties of a certain Gibbs model, the derived constraint and its numerical advantages are used in this thesis (see item 3). Finally, this thesis includes both the methods and problem formulations, as well as the case studies from [63, 60] (see items 4 and 6). All of the contributions of students and colleagues are given explicitly at the beginning of the respective section in this work.

In addition to the above given references, the author contributed to the following publications which do not form a part of this thesis:


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Notation

The following notation tables are not extensive but include the symbols most frequent in this work. Should a symbol be relevant to a particular chapter or section, it will be introduced when needed.

Latin Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A' \in \mathbb{R}^{MR \times N} )</td>
<td>stoichiometric matrix</td>
</tr>
<tr>
<td>( b \in \mathbb{R}^{MR} )</td>
<td>elemental abundance vector</td>
</tr>
</tbody>
</table>
| \( b\text{ceos}(x) \in \mathbb{R}^{P_{ph}} \) | covolume of CEOS, also \( b\text{ceos}(x_{ph}) \mathbb{R}_{>0} \)
| \( D(x_{ph}) \) | discriminant of a cubic equation |
| \( f(\cdot) \) | (upper-level) objective function |
| \( f\text{ceos}(\cdot) \) | cubic function, potentially cubic equations of state |
| \( G \) | molar Gibbs free energy for some reference state of formation |
| \( k_{a,ij} \in [-1, 1] \) | binary interaction CEOS parameter |
| \( LLP = \{1, \ldots, n_{llp}\} \) | index set of LLPs, \( LLP = LLP_1 \cup LLP_2 \cup LLP_3 \) |
| \( M_i \in \mathbb{R}_{>0} \) | constant for big-M formulation |
| \( n \in \mathbb{R}_{>0} \) | total molar amount of system |
| \( n_{i,ph} \in \mathbb{R}_{>0} \) | molar amount of species \( i \) in phase \( ph \) |
| \( n_{ph} \in \mathbb{R}_{>0} \) | total molar amount of system |
| \( n_{q} \in \mathbb{N}_{>0} \) | total number of thermodynamic model parameters |
| \( n_{l,llp} \in \mathbb{N}_{\geq 1} \) | total number of lower-level molar volume variables for \( llp \) |
| \( n_{u,llp} \in \mathbb{N}_{\geq 1} \) | total number of upper-level molar volume variables for \( llp \) |
| \( n_{l,llp} \in \mathbb{N}_{\geq 1} \) | total number of lower-level mole fraction variables for \( llp \) |
| \( \epsilon_{u,llp} \in \mathbb{N}_{\geq 1} \) | total number of upper-level mole fraction variables for \( llp \) |
| \( p \) | pressure |
| \( q^u \in \mathbb{Q}^u \subset \mathbb{R}^n_q \) | upper-level thermodynamic model parameters |
| \( r \) | universal gas constant |
| \( s \) | complementary slackness variable |
| \( TPD \) | temperature |
| \( T \) | temperature |
| \( v_{ph,r} \in \mathbb{R}_{>0}b\text{ceos}(x_{ph}) \) | tangent plane distance function |
| \( v_{l,llp} \in V_{l,llp} \subset \mathbb{R}^{n_{l,llp}} \) | molar volume of phase \( ph \) and root \( r \) |
| \( v_{u,llp} \in V_{u,llp} \subset \mathbb{R}^{n_{u,llp}} \) | lower-level molar volume for \( llp \) |
| \( v_r^{llp} \) | upper-level molar volume for \( llp \) |
| \( v_r^u \in V_u \subset \mathbb{R}^{n_{u,llp}} \) | upper-level molar volume for \( llp \) |
| \( v_r^\text{ph} \) | molar volume of root \( r \) of all phases satisfying CEOS |
| \( x_{l,llp} \in X_{l,llp} \subset [\epsilon, 1 - \epsilon]^{n_{l,llp}} \) | lower-level mole fraction for \( llp \) |
| \( x_{u,llp} \in X_{u,llp} \subset [\epsilon, 1 - \epsilon]^{n_{u,llp}} \) | upper-level mole fraction for \( llp \) |
Notation

\[ x^u \in X^u \subseteq [\epsilon, 1 - \epsilon]^{N_{llp}} \]
\[ x_{i,ph} \in [\epsilon, 1 - \epsilon] \]
\[ x_{ph} \in [\epsilon, 1 - \epsilon]^{N - 1} \]
\[ x \in [\epsilon, 1 - \epsilon]^{(N-1)Ph} \]
\[ \left( \frac{\partial }{ \partial x_i } \right)_{\hat{x},\hat{v}_r} \]
\[ \left( \frac{\partial }{ \partial v_r } \right)_{\hat{x},\hat{v}_r} \]
\[ Z_{ph,r} \in \mathbb{R}_{>0}(x_{ph}) \]

Greek Symbols

\[ \alpha \in [0.0, \alpha_{\text{max}}] \]
\[ \gamma_{i,ph} \]
\[ \Delta A \]
\[ \Delta G \]
\[ \Delta G^E \]
\[ \Delta \mu_{i,ph} \]
\[ \epsilon \]
\[ \theta \in \{0, 1\} \]
\[ \Theta(x) \]
\[ \lambda \]
\[ \mu_{i,ph} \]
\[ \nu \in \mathbb{R}^{N \times RC} \]
\[ \xi_{rc} \in [-1, 1] \]
\[ \tau_{ij} \]
\[ \Phi_{ph} \in [0, 1] \]
\[ \varphi_{i,ph} \in \mathbb{R}_{>0} \]

Super- and Subscripts

0
*  
\[ i = 1, \ldots, N \]
\[ j = 1, \ldots, MR \]
\[ l \]
\[ llp \]
\[ ph = 1, \ldots, Ph \]
\[ r \in \{1, 2, 3\} \]
\[ rc = 1, \ldots, RC \]
\[ t \]
\[ u \]
\[ v \]

superscript to denote feed
superscript to denote optimal point
subscript to denote species
subscript to denote reaction invariants
superscript to denote lower level
superscript to denote LLP
subscript to denote phase
subscript to denote real-valued root to cubic equation
subscript to denote chemical reaction
subscript to denote total amount
superscript to denote upper level
subscript to denote first derivative with respect to \( v_r \)
$vv$ subscript to denote second derivative with respect to $v_r$

**Abbreviations**

- **BLP**: bilevel program
- **BOARPET**: bilevel optimization algorithm for rigorous and robust parameter estimation in thermodynamics
- **CEOS**: cubic equation of state
- **DPP**: DECHEMA data preparation package
- **EC**: equality constraint
- **GAMS**: general algebraic modeling system
- **GN**: Gauss-Newton algorithm
- **(G)SIP**: generalized semi-infinite program
- **IC**: inequality constraint
- **KKT**: Karush-Kuhn-Tucker
- **LBP**: lower-bounding problem
- **LBD**: lower bound
- **LCST**: lower critical solution temperature
- **LHS**: left-hand side
- **(LI)CQ**: (linear independence) constraint qualification
- **LLP**: lower-level problem
- **LS**: least-squares error sum
- **MFCQ**: Mangasarian Fromovitz constraint qualification
- **(MI)NLP**: (mixed-integer) nonlinear program
- **MPEC**: mathematical program with equilibrium constraints
- **(M)THF**: (methyl)tetrahydrofuran
- **NRTL**: non-random two-liquid
- **PR**: Peng-Robinson
- **RHS**: right-hand side
- **(R)TPC**: (reactive) tangent plane criterion
- **(S)RK**: (Soave-)Redlich-Kwong
- **UBD**: upper bound
- **UCST**: upper critical solution temperature
- **UNIFAC**: universal quasichemical functional group activity coefficients
- **UNIQUAC**: universal quasichemical activity coefficients
- **UO**: unit operation
- **vdW**: van der Waals
- **VLE**: vapor-liquid equilibrium
- **(V)LLE**: (vapor-)liquid-liquid equilibrium
Kurzfassung


Wenngleich aufgrund der kommerziellen Unterlöser die Anwendbarkeit der neuen Methoden bisher auf illustrative Fallstudien beschränkt ist, zeigen die Studien dennoch, dass die globale gegenüber der gängigeren lokalen Optimierung insbesondere in der Thermodynamik einen unverzichtbaren Beitrag für die Industrie und universitäre Forschung leisten kann.
Abstract

In order to determine thermodynamic interactions in phase equilibria, there is an increasing interest in fully predictive methods. However, parameter estimation using measurement data often is more accurate and thus, still widely applied in the chemical industry. In this thesis, the parameter estimation problems in [108, 107, 20] are reinterpreted as bilevel problem (BLP) formulations and extended to different types of equilibria (phase, mechanical, and chemical reaction equilibria), and finally, solved by means of global deterministic optimization.

As an important feature of [108, 107, 20] and this thesis, thermodynamic stability is guaranteed to be satisfied for the regressed parameter values and the aforementioned equilibria, while standard regression tools fail. The key to the reliability of the new methods is the fact that they are appropriate for even nonconvex problems which are prevalent for thermodynamics, in that they use the algorithm in [110], in contrast to methods that perform a posteriori stability checks only, if any.

Numerical proofs for the importance of the satisfaction of thermodynamic stability are given, by comparing the BLP formulation to two prevalent specimens of regression tools, namely Aspen Data Regression System [8] and DECHEMA Data Preparation Package [1]. In particular, based on case studies of single-phase reactive systems and various liquid-liquid equilibria using the non-random two-liquid model, it is demonstrated that only the new methods reliably avoid, e.g., spurious phases and spurious liquid-liquid splits, as well as incorrect values for phase compositions and extents-of-reaction. In addition, for parameter estimation involving cubic equations of state models, a continuous criterion to discriminate between multiple roots to cubic equations is introduced in this thesis.

In terms of readership, this thesis tries to reach both the developers of said regression tools and process designers as their potential users. Even though the aforementioned case studies are predominantly illustrative in nature due to computational limits of the subsolvers used, the author believes that they demonstrably highlight the relevance of global optimization to process simulation and optimization in both academia and industry.
1 Introduction

Disclaimer: This chapter adopts parts of the section entitled “Introduction” from [63].

This thesis is concerned with parameter estimation in chemical reaction and phase equilibrium thermodynamics by means of methods in bilevel and global deterministic optimization. While fully predictive methods for (reaction) equilibrium thermodynamics are becoming progressively more powerful [51, 64, 165], data regression (parameter estimation) to equilibrium measurement data is, undeniably, still of great relevance to the chemical industry. This is evident from the wide variety of regression tools. For the last decades, a lot of research activities have been addressing parameter estimation in thermodynamics [54, 152, 159]. These consider, at best, rigorous a posteriori checks for thermodynamic stability with respect to the desired mole fractions, as well as spurious phase splits and spurious phases. In case thermodynamic stability is satisfied, the methods are rigorous and reliable [54, 152]. However, they lack a systematic strategy in the case of violation of thermodynamic stability.

In contrast, [108, 107, 20] interpret the parameter estimation problems in thermodynamics as generalized semi-infinite programs (GSIPs). The lower-level programs (LLPs) are closely related to the Gibbs free energy, a thermodynamic potential whose mathematical properties depend on the choice of the regressed thermodynamic model. The global minimization of the Gibbs free energy, i.e., the global solution of the LLPs in the GSIP, can be graphically interpreted by so-called tangent plane criteria [12, 154, 81, 80]. Although, with a few exceptions, the LLPs are nonconvex, the parameter estimation problems are commonly formulated as nonlinear programs (NLPs) by replacing the LLPs with their respective Karush-Kuhn-Tucker (KKT) conditions, in the literature and in (industrial) regression tools. Since solutions other than the global minimum of the Gibbs free energy may be found, this can lead to erroneous regression results and in essence, to a violation of thermodynamic stability. Unfortunately, in industry, such errors often do not surface with dispatch, that is, only upon usage in, e.g., process simulation and optimization.

In this thesis, existing parameter estimation problems for phase equilibrium are reinterpreted as bilevel problem (BLP) formulations, while new problem formulations are proposed for different types of equilibrium (mechanical and chemical reaction equilibrium). The solvers used are global deterministic optimization solvers.

In terms of readership, this thesis tries to predominantly reach both the software developers of the regression tools and process designers as their potential users. Therefore, this thesis’ structure is as follows: In Chapter 2, thermodynamic stability for stable systems is interpreted by KKT theory as given in the literature, and its importance to parameter estimation is highlighted. Next, complementing [108, 107, 20] on activity coefficient models for nonreactive systems, the implementation of the bilevel algorithm in [110] in the regression tool BOARPET is outlined in Chapter 3, and regression results for liquid-liquid equilibrium (LLE) fluid systems relevant to future biorefinery processes and/or current industrial applications are presented. Further, prominent implementations of said inadmissible NLP reformulations and undesired issues that they entail are discussed. Their
1 Introduction

interference with potential industrial process simulation results is revealed, and for Aspen Data Regression System (DRS) [8], arguably the most prevalent tool, the root of the problem is demonstrated by a formal proof. As an extension of [108, 107, 20], BLP formulations for regressing activity coefficient models in reactive systems and cubic equations of state (CEOS) are proposed in Chapters 4 and 5, respectively. A particular focus is laid on the problem variables since the LLPs do not only comprise mole fractions as in [108, 107, 20] but additionally, certain KKT multipliers, molar amounts and molar volumes. As a special feature, the BLP formulation for the regression of CEOS includes a continuous root discrimination criterion that is based on Cardano’s formula. The advantages of the BLP over standard formulations, e.g., the well-known equilibrium constant method, is demonstrated by means of illustrative case studies, and the consequences for process design are discussed. Finally, conclusions, potential impact of this thesis, and outlook follow in Chapter 6.

It should be noted that thermal stability is assumed to be satisfied throughout this thesis. Similarly, model and parameter identifiability, as well as unstable and metastable equilibrium states are not in the scope of this thesis. The reason for not covering the first is that some of the established models are semi-empirical, e.g., [142]. Thus, by model definition, there is no obvious way to draw physical conclusions from the respective parameter values, irrespective of their structural (non)identifiability. In terms of practical nonidentifiability, it is ad hoc left to the engineer to provide sufficient measurement data. Finally, metastable und unstable states are deemed less relevant to the chemical industry and often are endowed with little measurement data.
2 Need for Bilevel Programming in Thermodynamics

Disclaimer: This chapter adopts parts of the section entitled “Introduction” from [63].

The model of the thermodynamic potential under consideration, e.g., the Gibbs free energy function, exhibits certain parameters which may be empirical or physically meaningful. These parameters are unknown a priori and thus, are commonly determined by parameter regression from measurement data. As a special feature, the bilevel problem (BLP) that will be introduced shortly captures the fact that only those parameter values are feasible that imply Gibbs free energy curves satisfying thermodynamic stability. Since this is represented by semi-infinite constraints [12, 154, 81] and/or LLPs to the regression problem, in general, there is no nonlinear program (NLP) which is less costly, yet mathematically equivalent to the numerically demanding BLP. The special case of convex LLPs is an exception, in which the equivalence may be established due to the guarantees of the Karush-Kuhn-Tucker (KKT) second-order sufficient conditions, e.g., [17]. However, in the literature and in (industrial) regression tools, the parameter estimation problems are formulated as NLPs throughout, at best, by replacing the LLPs with their respective KKT conditions, cf. Sections 3.2 and 3.3. In these cases, points other than even local minima of the Gibbs free energy may be found, demonstrably affecting subsequent flowsheeting and simulation results upon usage of the respective parameter values.

This chapter presents the well-known rule of thermodynamic stability which is analyzed by KKT theory in Section 2.1, followed by the introduction of the BLP formulation in Section 2.2. Next, the need for bilevel programming is discussed in terms of convexity of the lower-level problem (LLP) in Section 2.3, and by giving evidence of failures of the standard methods in Section 2.4. In Appendix A.1, we discuss the conditions under which the reactive tangent plane criterion (RTPC) is fully applicable (stand-alone), while a BLP with a mathematical program with equilibrium constraints (MPEC) in the upper level and its relevance to parameter estimation are discussed in Appendix A.2. Finally, Appendix B presents a short formal proof for convex problems in phase equilibria.

2.1 Thermodynamic Stability

Disclaimer: This section adopts parts of the section entitled “Criteria for thermodynamic stability” from [63].

In the author’s publications related to this thesis, we refer to the stable equilibrium as the Second Law of thermodynamics. In particular, we focus on $T, P = \text{const}.$ and thus, minimization of Gibbs free energy. This is in accordance with, e.g., [154]. Other authors state the Second Law only in terms of entropy maximization and then use the First Law to derive the equilibrium condition, e.g., [162]. For clarity, in this thesis, we will refer to the stable equilibrium as thermodynamic stability.
Theorem 1 (Thermodynamic stability) At a given temperature $T$ and pressure $P$, a thermodynamic state is stable iff the total Gibbs free energy $nG$ of the respective thermodynamic system is minimal with respect to all fluctuations, subject to atom balance.

Equivalent theorems also exist for thermodynamic potentials other than the Gibbs free energy, and different choices of variables are conceivable. (Thermal stability is assumed throughout this thesis.) For instance, for the molar Gibbs free energy $G$ relative to some reference state of formation, [154, Equations 1 to 6] propose

$$
\min_{n, x} \left( nG(x, q) = \sum_{ph} n_{ph} G_{ph}(x_{ph}, q) = \sum_{ph} n_{ph} \sum_i x_{i,ph} \mu_{i,ph} (x_{ph}, q) \right) (2.1a)
$$

s.t. \sum_{ph} n_{ph} \sum_i x_{i,ph} A'_{ji} - b_j = 0, \ \forall j \quad (2.1b)

\sum_i x_{i,ph} - 1 = 0, \ \forall ph, \quad (2.1c)

where $j = 1, \ldots, MR$ is the index of reaction invariants, e.g., chemical elements, $i = 1, \ldots, N$ the index of species, and $ph = 1, \ldots, Ph$ the index of phases. Further, $n \in \mathbb{R}_{>0}^{Ph}$ denotes the molar amount, $n \in \mathbb{R}_{>0}, n = \sum_{ph} n_{ph}$ the total molar amount of the system, $q \in \mathbb{R}^{Q}$ the constant parameters of the thermodynamic model of $G$, and $\mu \in \mathbb{R}^{N \times Ph}$ and $x \in (0,1)^{N \times Ph}$ the chemical potential and mole fraction, respectively. Finally, $A' \in \mathbb{R}_{>0}^{MR \times N}$ and $b \in \mathbb{R}_{>0}^{MR}$ represent the stoichiometric matrix and the elemental abundance vector, respectively.

To this point, we have assumed that Problem (2.1) is feasible and well-posed, in the sense that $A'$ has full rank; if, however, rank($A'$) < MR, certain measures are required, cf. Appendix A.1. Furthermore, the original formulation in [154] comprises additional complementarity slackness conditions which allow vanishing and reappearing phases; why they can be omitted in our case is briefly discussed in Appendix A.2. In addition, throughout this thesis, we assume that for a given optimization problem the feasible set is nonempty and compact and thus, Weierstrass’ theorem holds and the minimum is attained. Finally, let the linear independence constraint qualification (LICQ) be satisfied such that KKT theory is fully applicable, unless indicated otherwise.

In the trivial case of no chemical reaction, it holds $n = const.$ and $A = I$, where $I$ is the identity matrix [80]. Then, the atom balance (Equation (2.1b)) becomes a simple mass balance, cf. e.g., [154], given by

$$
\sum_{ph} n_{ph} x_{i,ph} - n_{i}^0 = 0, \ \forall i = 1, \ldots, N, \quad (2.2)
$$

where $n_{i}^0 \in \mathbb{R}_{>0}$ denotes the molar amount of species $i$ in the feed. For a different choice of variable space, also see Problem (E.1).

2.1.1 Tangent Plane Criteria

A KKT point of Problem (2.1) denoted by $(\ast)$ satisfies [154]

$$
\mu^{\ast}_{i,ph} (x^{\ast}_{ph}, q) - \sum_j \lambda^{\ast}_j A'_{ji} = 0, \ \forall ph, i \quad (2.3a)
$$
2.1 Thermodynamic Stability

\[ \sum_{ph} n_{ph}^* \sum_i x_{i,ph}^* A_{ji} - b_j = 0, \quad \forall j \]  
\[ \sum_i x_{i,ph}^* - 1 = 0, \quad \forall ph, \]  
(2.1b, 2.1c)

where \( \lambda \in \mathbb{R}^{MR} \) denotes the Lagrangian multiplier. By means of such a KKT point [154, Equation 23] reformulate Problem (2.1) to

\[ n^* G^*(x^*, q) \leq \tilde{n} G(\bar{x}, \bar{q}), \]  
(2.4)

\( \forall (\bar{x}, \bar{q}) \) feasible in Problem (2.1), in order to derive a so-called tangent plane criterion. Said criterion provides the same mathematical guarantees as Problem (2.1), i.e., it is both sufficient and necessary for thermodynamic stability; however, it has some added advantages. The most compelling of which arguably are

1. it is a semi-infinite condition and
2. under appropriate assumptions, it allows to graphically validate that the global minimizer of \( nG(x, q) \) has actually been found.

**Theorem 2** (Reactive) Tangent Plane Criteria (RTPC, TPC) of Baker, Smith, and Jiang [12, 154, 81, 80] Suppose that Problem (2.1) is feasible and that Weierstrass’ theorem and LICQ hold, cf. Appendix A.1. Then, a KKT point is a global minimizer iff the common tangent plane \( \Theta(x) \) to the molar Gibbs free energy \( G(x, q) \) is a supporting hyperplane for given \( T, P \), that is,

\[ G(\bar{x}, \bar{q}) - \Theta(\bar{x}) \geq 0, \quad \forall \bar{x} \in (0, 1)^{N-1}. \]  
(2.5)

**Remarks:**

- As a consequence of Theorem 1, thermodynamic stability is satisfied iff Equation (2.5) holds.
- As an implication of Theorem 2, the number of points of tangency is equivalent to the number of phases. That is, for \( \bar{X} = \{\bar{x} : G(\bar{x}, \bar{q}) - \Theta(\bar{x}) = 0\} \), we have \( \text{card}(\bar{X}) = Ph \).
- Equation (2.5) often is used in the form [154, Equation 26]

\[ \sum_{ph} n_{ph} \sum_i x_{i,ph} (\mu_{i,ph}(x_{ph}) - \mu_{i,ph}^*) \geq 0, \]  
\[ \forall (x, n_{ph}) \) feasible in Problem (2.1). \]  
(2.6)

Theorem 2 also implies certain criteria for spurious phase splits and phases [107]. Figure 2.1 shows the different types of violation of thermodynamic stability. Most importantly, it illustrates that the sufficient criterion (semi-infinity) can be violated while the necessary ones are satisfied, cf. Chapter 3.

### 2.1.2 Necessary Criteria for Thermodynamic Stability

Applying the KKT first-order conditions of Problem (2.1), cf. Equation (2.3a), to a two-phase system yields

\[ \mu_{i,ph}^* (x_{ph1}^*, q) = \mu_{i,ph2}^* (x_{ph2}^*, q), \quad \forall i, \]  
(2.7)
which is the prominent isopotential criterion for phase equilibrium the basis of the pop-
ular Rachford-Rice equation. On the other hand, for a particular phase, Equation (2.3a) 
together with \( \mathbf{A}^\prime \nu_{rc} = \mathbf{0}, \; \forall rc, \; \nu_{rc} \neq \mathbf{0} \), results in the well-known chemical reaction equi-
librium constant which reads

\[
\sum_i \nu_{i,rc} \mu^*_{i,ph}(\mathbf{x}_{ph}, \mathbf{q}) = 0, \quad \forall rc,
\]

(2.8)

where \( rc = 1, \ldots, RC \) denotes the index of independent chemical reactions and \( \nu \in \mathbb{R}^{N \times RC} \) 
the stoichiometric coefficients, cf. Appendix G.1. (For the specific case of an ideal mixture, 
Equation (2.8) is also often referred to as the well-known mass action law.) Equations 
(2.7) and (2.8) or variations, such as chemical reaction equilibrium constants, are based 
on KKT conditions only and give, thus, a necessary but not a sufficient criterion for the 
satisfaction of thermodynamic stability. As an advantage, however, they are not semi-
infinite conditions, and Lagrange multipliers \( \lambda_j \) are not explicitly required [162].

2.1.3 KKT Second-Order Necessary Condition

In addition to the KKT first-order conditions of Problem (2.1), cf. Equation (2.3), the 
second-order necessary condition derived by [81] reads

\[
H(\mathbf{x}^*, \mathbf{q}) \geq 0,
\]

(2.9)

i.e., the Hessian \( H \) of \( G(\mathbf{x}, \mathbf{q}) \) with respect to \( \mathbf{x} \) be positive semi-definite at \( (\mathbf{x}^*, \mathbf{q}) \). Con-
sequently, a point \( \mathbf{x}^* \) which satisfies the (R)TPC (2.5) in addition to respective constraint 
qualifications (CQs), cf. Appendix A.1, also satisfies Equation (2.9).

2.2 Proposed Bilevel Program

Disclaimer: This section adopts the introduction, the problem statement and related explanations from 
the section entitled “Proposed bilevel program” in [63], which were each slightly adapted to fit a more 
generic problem statement in this thesis. Furthermore, Figure 2.1 which was created by the author is taken 
from [60].

To this point, the thermodynamic parameters \( \mathbf{q} \) were assumed constant. During the param-
eter regression, however, these become optimization variables and typically are determined 
by minimizing the model-experiment mismatch using suitable thermodynamic models. The 
achievement in [107, 108, 20] is to embed thermodynamic stability (Problem (2.1)), in said 
regression.

One option to encode thermodynamic stability as a sufficient requirement on stability is 
Equation (2.5) representing a semi-infinite constraint to parameter regression. Thus, the 
regression program may be interpreted either as a semi-infinite program (SIP) [107] or as 
a BLP, depending on the communication between the objective and the constraints. In 
this work, the latter is chosen, as for some of the LLPs (cf. a) in the following), it is the 
minimizer of the LLP which is required in the upper level, while for others (cf. b to d) in 
the following), it is the optimal objective function value of the lower level. The resulting 
BLP comprises an upper-level (parameter fitting) problem, along with several nonconvex 
LLPs. The latter ensure a) the fulfilment of thermodynamic stability of the predicted mole
fractions satisfying the (R)TPC, as well as \( b \) the same number of phases and \( c \), \( d \) the same number of phase splits as observed in the experiments. A simplified structure of the BLP is given by Problem (2.10)

\[
\begin{align*}
\min_{x^u, q^u} & \quad f^u(x^u, q^u) \quad \text{(2.10a)} \\
\text{s.t. } & \quad h^u(x^u, q^u) = 0 \quad \text{(2.10b)} \\
& \quad g^u(x^u, q^u) \leq 0 \quad \text{(2.10c)} \\
& \quad -f^{l,lp}(x^{u,lp}, q^u) \leq 0 \\
& \quad x^{u,lp} \in \text{argmin}_{x^{l,lp}} f^{l,lp}(x^{l,lp}, q^u) \\
& \quad \text{s.t. } g^{l,lp}(x^u, x^{l,lp}) \leq 0 \\
& \quad \forall llp \in LLP \quad \text{(2.10d)} \\
\end{align*}
\]

where \( x^{l,lp} \) denotes the lower-level mole fraction variables, \( x^{u,lp} \) and \( x^u \) the upper-level mole fraction variables, and \( q^u \) the Gibbs free energy model parameters which are the degrees of freedom in the parameter estimation. Equation (2.10a) may represent, e.g., a least-squares error sum (LS) to indicate the goodness of fit. Equation (2.10b) encodes the KKT first-order conditions of Problem (2.1); the primal feasibility conditions are represented by Equation (2.1b) or (2.2), and (2.1c), while the stationarity conditions are delineated by Equation (2.3a) or related forms, such as (2.8) and (2.7), respectively. Furthermore, Equation (2.10d) casts the (R)TPC as a nonconvex LLP. As this may be repeated for each datum to which the regression is conducted, a set \( LLP \) of multiple LLPs in parallel evolves. Similarly, the criteria \( b \) to \( d \) may each be formulated as such an LLP. Finally, Equation (2.10c) can be considered an optional inequality constraint (IC), e.g., in the form of Equation (2.9).

In order to obtain only those parameter values \( q^u \), i.e., shapes of the Gibbs free energy, cf. Figure 2.1, that correspond to a bilevel-feasible solution, it is indispensable to solve all of the (nonconvex) LLPs to global optimality. Fortunately, \( g^{l,lp}(x^u, \cdot) \) are simple linear constraints. Therefore, the solution of the BLP can be performed according to a simplified version of [110], yet it can be numerically challenging.

### 2.3 (Non)Convexity

The convexity properties of the LLPs depend on the choice of their variables. However, discussing the most appropriate choice with respect to convexity of the LLPs is omitted here for brevity. It should be noted that convexity of an optimization problem is a sufficient, yet not a necessary condition for its unimodality. In general terms, we will find that Problem (2.1) is multimodal and nonconvex so that the satisfaction of LLP (2.10d) cannot be guaranteed with local optimizers only; on the contrary, the nonconvex LLPs need to be solved by global optimizers, in order to find bilevel-feasible points that are solutions of Problem (2.10).

Under appropriate assumptions, however, the satisfaction of (2.10d) can be guaranteed a priori for certain LLPs, so that solving the respective LLPs can be omitted and the solution of Problem (2.10) becomes less costly. This is shown in Appendix B. These assumptions are closely related to the convexity properties of the applied thermodynamic
Fig. 2.1: Schematics of Gibbs free energy $\Delta G$ with respect to mole fraction $x_{i,ph} \in (0, 1)$ for binary vapor-liquid equilibrium (VLE) at $T,P = \text{const.}$ showing options of violating thermodynamic stability. Dashed declining lines: tangent predicted by model, dashed vertical lines: phase compositions predicted by model, shaded areas: violation of Baker’s criterion [12] or other undesired behavior. a: violation of Baker’s criterion, b: violation of correct number of phases, c: violation of correct number of phase splits due to local nonconvexity of lowest curve, d: violation of correct number of phase splits due to change of curves. Different phase equilibrium types, e.g., vapor-liquid-liquid equilibria (VLLE), are analogous; the two phases can be exchanged. Proposed BLP (2.10) and the generalized semi-infinite program (GSIP) in [108, 107, 20] exclude all violations.
models of the Gibbs free energy, specifically the partial convexity of molar the Gibbs free energy $\Delta G$ relative to the reference state "pure, real liquid" or "pure species at ideal gas state", $\Delta G_{ph}(x, q)$ in mole fraction $x$ on $X = (0, 1)^{N-1}$. The convexity properties of $\min\{\Delta G_1, \ldots, \Delta G_{ph}, \ldots, \Delta G_{Ph}\}$, and its convex hull are of particular interest, cf. e.g., [66, 106].

In the following sections, we investigate for which Gibbs free energy models the assumption in Appendix B, at least, partially holds. If it does, the costs of solving Problems (2.10) and (2.1) might be significantly reduced.

### 2.3.1 Convexity Properties of the Model of Ruszczyński et al.

**Disclaimer:** This section is reprinted (adapted) with permission from Glass and Mitsos. Comment on “Reliable Correlation for Liquid-Liquid Equilibria outside the Critical Region”. J. Chem. Eng. Data, 2017 (62), 4041-4042, [61]. Copyright (2017) American Chemical Society.

In this section, the convexity properties of a specific model proposed in [144] shall be analyzed, adopting the respective notation. In terms of modeling, fluctuation solution theory provides models for liquid-liquid equilibria (LLE) by a Maclaurin series expansion, i.e., a Taylor series expansion at zero, based on the Porter model, e.g., [34, 144]. Zero is a particularly appropriate base point of such a series expansion, provided it is applied to modeling rational activity coefficients as proposed in [118]. [144] apply such a model to binary LLE exhibiting phases $ph_1$, $ph_2$, and use a regression method which considers only necessary criteria for stability. It should be noted that, as opposed to using the same energy model for both phases in equilibrium, one can superimpose two (convex) sub-models, e.g., Wilson with ideal gas for VLE and asymmetric models for ionic liquid systems [151].

From [144, Equation (15)] it follows that the reduced molar Gibbs free energies of the proposed model can be written as

$$\frac{\Delta G_{ph_1}}{RT} = x_{ph_1} (\ln x_{ph_1} + \ln \gamma_{1,ph_1}) + (1 - x_{ph_1})(\ln(1 - x_{ph_1}) + \ln \gamma_{2,ph_1} + \ln \gamma_{rat}) \quad (2.11)$$

$$\frac{\Delta G_{ph_2}}{RT} = x_{ph_2} (\ln x_{ph_2} + \ln \gamma_{1,ph_2} + \ln \gamma_{2,ph_2}) + (1 - x_{ph_2})(\ln(1 - x_{ph_2}) + \ln \gamma_{2,ph_2}), \quad (2.12)$$

where $x_{(ph_1, ph_2)} \in X = (0, 1)$ denotes the mole fraction, $T \in \mathbb{R}_{>0}$ the temperature in K, $\gamma_{i,(ph_1, ph_2)}^{\infty}$ the activity coefficient at infinite dilution, and $\gamma_{i,(ph_1, ph_2)}^{rat}$ the rational activity coefficient of species $i$ (also known as unsymmetric convention activity coefficient). Since with [144, Equations (9)-(14)],

$$\frac{1}{RT} \frac{\partial^2 \Delta G_{(ph_1, ph_2)}}{\partial (x_{(ph_1, ph_2)})^2} = \frac{2c_{(ph_1, ph_2)}(x_{(ph_1, ph_2)} - (x_{(ph_1, ph_2)})^2)}{Tx_{(ph_1, ph_2)}(1 - x_{(ph_1, ph_2)})} + T \quad (2.13)$$

and

$$\max_{x_{(ph_1, ph_2)} \in X} x_{(ph_1, ph_2)} - (x_{(ph_1, ph_2)})^2 = 0.25, \quad (2.14)$$

$1/(RT) \cdot \Delta G_{(ph_1, ph_2)}(\cdot, T)$ is partially convex in $x_{(ph_1, ph_2)}$ on $X$ iff $c_{(ph_1, ph_2)} > -2T$ (also see, e.g., [29, 74, 36] for a comparable result for the Porter model; [144] use the model in [34].
but truncate the Maclaurin series after the first term which essentially gives a Porter-like
activity coefficient model). This is complementary to the condition \( c_{(ph_1, ph_2)} < 0 \) proposed
to ensure the desired sign of derivatives of activity coefficients with respect to composition
(mentioned as “phase stability” [144, Table 1]). For truncation of the Maclaurin series
after terms of higher orders, these results do not necessarily hold. In addition, we focus
on binary systems, while for multi-component mixtures certain revisions are likely to be
required.
Provided that \( c_{(ph_1, ph_2)} > -2T \), flash calculations are facilitated since isopotential (2.7)
is sufficient for Baker’s criterion, giving a system of nonlinear equations as opposed to an
NLP (2.1). The use of the proposed Gibbs models [144] for process simulation is, thus,
simplified. Perhaps more importantly, during the parameter estimation the correct number
of phases and Baker’s criterion are met as long as isopotential is satisfied. (It should be
noted, however, that this does not guarantee the correct number of phase splits; for a
counter example, see Figure 2.1).
Consequently, the demanding nonstandard programs for parameter estimation [108, 107, 20]
can be simplified by imposing \( c_{(ph_1, ph_2)} > -2T \) as a constraint within the regression formulation. It should be noted that the condition is
sufficient but not necessary for satisfying Baker’s criterion. Should it entail the exclusion
of physically meaningful parameter values, and should this disadvantage of the criterion
outweigh its favorable guarantee, then Baker’s criterion will need to be satisfied by some
other probably more involved means during the regression, and, at least, a posteriori checks
are required.
Finally, the reported regression method [34, 144] could also benefit from regressing all of the
parameters simultaneously, in addition to using global solvers to obtain the best possible
fit upon convergence. The reason for this is that regressing a subset of the parameters
does not even guarantee a locally optimal fit.
In particular, it can be shown [61] for the LLE of octanol/water, which is comparable to
the case studies in [144] in terms of breadth of the miscibility gap that the total modeling
and computational effort are rather low. These include constraining the parameter space
to \(-2T < c_{(ph_1, ph_2)} < 0\), regressing all of the parameters simultaneously, and using the
established deterministic global solver BARON 17.4.1 [161]. The LLE of octanol/water
serves as an example to demonstrate the straightforward applicability of the proposed
constraint.

### 2.3.2 Convexity Properties of Established Models

Besides the Gibbs free energy model discussed in Section 2.3.1, there are several established
models, for which, fortunately, the thermodynamic literature is abundant in investigations
on their respective convexity properties. However, these often are no mathematical proofs;
the statement that a certain thermodynamic model causes nonconvexity of the Gibbs free
energy or a related potential, in the thermodynamic literature, often is implied by reporting
“multiplicity” of solutions [29, 123, 74, 56, 22] and the capability of representing LLEs,
e.g., [130]. In a few cases, somewhat more mathematical investigations can be found. The
findings that are deemed most important for this thesis are summarized in Table 2.3.2.
If convexity of a certain model in \( x \) on \((0, 1)\) can be established, then the simplifications
outlined in Section 2.3.1 can be exploited. If, however, a certain model is nonconvex, the
KKT conditions of Problem (2.1) are not sufficient for its global minimizer. Consequently,
if Problem (2.10) is solved without Equation (2.10d), then spurious phases and phase splits
2.4 State-of-the-Art Parameter Estimation Tools

Table 2.1: Investigations of convexity of $G_{ph}$ and $\Delta G_{ph}$ in $x$ on $(0, 1)$ for binary systems in the literature.

<table>
<thead>
<tr>
<th>Gibbs model/system</th>
<th>Statement</th>
<th>Quality</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal nonreactive</td>
<td>convex</td>
<td>proof</td>
<td>[98, 29, Prop. 3.1]</td>
</tr>
<tr>
<td>Ideal reactive</td>
<td>strictly convex</td>
<td>proof</td>
<td>[155]</td>
</tr>
<tr>
<td>$\gamma, \varphi = \text{const.}$, nonreactive</td>
<td>strictly convex</td>
<td>discussion</td>
<td>[101]</td>
</tr>
<tr>
<td>$\gamma, \varphi = \text{const.}$, reactive</td>
<td>convex</td>
<td>discussion</td>
<td>[101, 14, 131]</td>
</tr>
<tr>
<td>Wilson</td>
<td>convex</td>
<td>proof</td>
<td>[98]</td>
</tr>
<tr>
<td>Model in [144]</td>
<td>cond. convex</td>
<td>proof</td>
<td>[61], 2.3.1</td>
</tr>
<tr>
<td>Porter*</td>
<td>cond. convex</td>
<td>proof</td>
<td>[36, 29, 74, p. 591]</td>
</tr>
<tr>
<td>Two-constant Margules</td>
<td>cond. convex</td>
<td>discussion</td>
<td>[29]</td>
</tr>
<tr>
<td>Two-constant van Laar</td>
<td>cond. convex</td>
<td>discussion</td>
<td>[29]</td>
</tr>
<tr>
<td>Model of Lewis &amp; Randall</td>
<td>cond. convex</td>
<td>proof</td>
<td>[123]</td>
</tr>
<tr>
<td>PR, SRK, vdW</td>
<td>(non)convex terms</td>
<td>discussion</td>
<td>[72, 49, 87]</td>
</tr>
<tr>
<td>NRTL, UNIQUAC</td>
<td>(non)convex terms</td>
<td>proof</td>
<td>[97]</td>
</tr>
<tr>
<td>UNIFAC, ASOG</td>
<td>(non)convex terms</td>
<td>proof</td>
<td>[98]</td>
</tr>
</tbody>
</table>

* one-constant Margules

can occur as reported in [74], as well as a violation of the (R)TPC. This calls for the costly solution of the full BLP (2.10) in regression, and the global solution of Problem (2.1) in the process simulation. In fact, from Table 2.3.2 it seems that it is the nonconvex cases that are most prevalent. In the following chapters, we will highlight the need for global optimization for the nonconvex non-random two-liquid model (NRTL) and the two-constant Margules model, and also discuss Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) models.

2.4 State-of-the-Art Parameter Estimation Tools

We are predominantly interested in the desirable guarantees, with which a certain regression tool will find a bilevel-feasible solution $(x^u, \hat{x})$ of Problem (2.10), and a certain unit operation (UO) model will regain that very solution $x^u$ upon use of $q^u$. As an aside, we also briefly discuss the ability of a tool to find a global minimizer of $f^u$.

To date, established regression tools, prevalent for industry and academia [8, 3, 45, 1], are based on local optimization only. As a consequence, they usually do not guarantee a bilevel-feasible point $(x^u, \hat{x})$. Similarly, today’s UO models in process simulators, such as reactor and flash models, commonly implement variations of Problem (2.1) and attempt to solve it globally by means of local solvers and sophisticated initialization strategies [23, 24, 42, 56, 57, 58, 90, 124, 147, 150, 174]. In the context of Problem (2.10), such UO models can, thus, often be represented by a nonlinear equations system. It combines Equation (2.10b) with (2.10c) and in this sense, the UO model and certain parts of the regression Problem (2.10) become identical.

The fact that UO models and/or regression tools rely on local optimization can lead to considerable errors in the process simulation and optimization. For instance, the UO model could erroneously be using $\hat{x} \neq x^u$. One reason for this to occur could be the local nature of its own solver, that is, for a given $q^u$, the UO model is not able to recreate the global minimizer $x^u$ because it is misled by some local solution $\hat{x}$. This would clearly be the
failure of the UO model, yet not the regression tool. Another, less obvious reason is the case in which the regression tool passes some infeasible parameters \( \hat{q} \neq q^{\ast,\ast} \) to the UO model. Then, the UO model might even find the global minimizer \( \hat{x} \) corresponding to \( \hat{q} \). However, this would not lead to the desired solution since generally \( \hat{x} \neq x^{\ast,\ast} \), and would be attributed to a failure of the regression tool.

In any case, the process simulator would use phase compositions and phases other than what is evident from experiments (provided the regression results in a good fit). Unfortunately, these errors can be both quantitative and qualitative in nature, cf. Section 3, and can considerably affect engineering results in practice. A “complete” set of measurement data of the respective fluid system can only reduce the risk of such errors. The urge to avoid them with mathematical guarantee calls for UO models and regression tools which both would rely on global optimization. Admittedly, this can be very costly compared to local methods. Unfortunately, however, some standard tools do not even seem to implement local minimization reliably, as we will show shortly. A list of major errors is given as follows, some of which will be discussed in the remainder of this thesis:

1. [93] demonstrate violation of the KKT first-order conditions (Equation (2.10b)) in CHEMCAD [2] which is prevalent for the process simulation in industry and academia. Such violations can occur when, e.g., Equation (2.10b) is treated as a pair of ICs or by means of a penalty method.

2. The author and coworkers [59] prove violation of the KKT second-order sufficient conditions (Equation (2.10c)) in Aspen DRS [8], a sub-tool of the world’s leading process simulator Aspen Plus [7, 52]. The resulting quantitative error, i.e., incorrect numerical values for the phase composition, is highlighted for a representative UO model, also see Section 3.3. The follow-up [26], as well as [94] reveal some further distinct violations of thermodynamic stability, both in Aspen DRS and the UO models in Aspen Plus.

3. In Section 3.2, we demonstrate the violation of Equation (2.10d) for the LLP corresponding to Figure 2.1d. We use Gauss-Newton through DECEMHA Data Preparation Package (DPP) [1], a local solver for generic QPs from least-square error regression. The resulting qualitative error, i.e., incorrect phase equilibrium phenomena, is highlighted for representative UO models and fluid systems in [26]. [148] make similar observations in Aspen DRS, cf. Chapter 5.

4. Failures to find a global minimizer of Problem (2.10), i.e., a globally best fit are discussed elsewhere, e.g., [54, 53, 44, 21].

The above given list illustrates that any type of erroneous result, infeasible or sub-optimal to Problem (2.10), is obtained in practice due to local methods. In contrast, the regression tool BOARPET [109] (Bilevel Optimization Algorithm for Rigorous and Robust Parameter Estimation in Thermodynamics) relies on global optimization and is based on [20, 108, 107]. For a comparison of BOARPET to two of the above listed standard tools, see the following chapter.
3 Parameter Estimation of Activity Coefficient Models in Nonreactive Systems

[108, 107, 20] propose a formulation of the parameter estimation problem as a generalized semi-infinite program (GSIP), for activity coefficient models in nonreactive systems. The program exhibits nonconvex LLPs, owing to the mathematical properties of these models, cf. Section 2.3, and is solved by a variation of the algorithm in [110]. Therefore, this chapter is structured as follows:

Section 3.1 presents extensions of the implementation of Mitsos, the tool BOARPET [109]. Two thermodynamic case studies which arise from extraction processes in future biorefineries, tetrahydrofuran (THF)/water and butanole (ButOH)/water, are used to demonstrate the advantages of BOARPET over a standard regression tool. In particular, in Section 3.2, it is shown that the Gauss-Newton solver which is prevalent for generic regression problems, is misled by an infeasible point of Problem (2.10). Section 3.3 is based on [59] and the fluid system 2-methyltetrahydrofuran (2MTHF)/water; it covers a related issue with Aspen DRS, a sub-tool of the world’s leading process simulator Aspen Plus, which to date, is unresolved, yet of great importance to the (industrial) user as we will show shortly. In particular, we demonstrate that the solver erroneously reports an infeasible point of Problem (2.10), as it violates thermodynamic stability. This chapter concludes with Section 3.4 by presenting NRTL [142] parameters that are generated by BOARPET and might play an important role in identifying promising candidates for future biorefinery extraction systems. These include the system 3-methyltetrahydrofuran (3MTHF)/water, based on [88], and further systems investigated in the excellence cluster Tailor-Made Fuels from Biomass (TMFB).

3.1 BOARPET

Disclaimer: This section adopts the description of the algorithm in [110] from [60]. Contributions to the BOARPET code: Alexander Mitsos wrote the first BOARPET version for parameter estimation of activity coefficient models in nonreactive systems [108, 107, 20]. Tjalf Hoffmann substantially contributed to restructuring the code, assisted with improving it for the parameter estimation of activity coefficient models in nonreactive systems, and wrote the interface to DEHEMA DPP. Johannes-Robert Bruch, Pablo Valero Cabeza and Clemens Fricke each coded particular BOARPET features as indicated in the BOARPET source files, in the course of their student’s jobs and/or Master’s theses [26, 166]. The features written by Bruch and Fricke, in most cases, are not essential when using the code. All of the changes to the code, except for its first creation, were undertaken under the guidance of the author or by the author herself. Some of the author’s major contributions are listed below, in addition to those of Valero Cabeza and Hoffmann, as indicated.
BOARPET (bilevel algorithm for rigorous and robust parameter estimation in thermodynamics) implements a variation of [110] and the methods published in [108, 107, 20, 59]. The algorithm in [110] uses a discretization method according to which a relaxation of Problem (2.10), a so-called lower-bounding problem (LBP) is solved followed by all LLPs (2.10d). If the constraints on the optimal objective function values of the LLPs are satisfied, the algorithm terminates, else the LBP is tightened. In particular, constraints are imposed that approximate the optimal objective functions of the LLPs. In terms of software architecture, BOARPET is essentially C++ code calling BARON [161] and other solvers through the General Algebraic Modeling System (GAMS). In the course of the author’s PhD, the original code provided by Mitsos was restructured and extended to said computational tool. In particular, the following major extensions were made:

- With the help of Hoffmann, implementation of the algorithm in [110] adapted to the parameter estimation problem (2.10). The fact that the lower-level constraints are simple linear functions greatly simplifies the application of the respective algorithm. Particular focus was laid on the adaptation of tolerance settings from [110], as well as on the structuring of the sets to collect constraint violations.

- Improvement of the formulation of the LBP, as well as reformulation and addition of particular LLPs. This allows for a reduction of second-order derivatives of the Gibbs free energy to first-order derivatives, yet coming with an increased number of lower-level variables, as explained in [60].

- Extension to parameter estimation of cubic equations of state (CEOS) models, cf. Section 5 and [62, 60].

- With particular focus on VLLE, extension from two-phase to multi-phase systems, i.e., three and more coexisting phases.

- With particular focus on LLE, extension to handling erroneous trivial solutions, degenerated Gibbs free energies and incomplete industrial measurement data, by adding certain constraints to the LBP and linear inter- and extrapolation to generate pseudo data, respectively, with substantial contributions of Valero Cabeza [166].

- The logical constraints in [110] as required for the problem formulation in [107] were hard-coded in the original code provided by Mitsos. As a drawback, complete measurement data were required, in order to discretize the lower-level variable space. Since industrial case studies often do not exhibit such a complete data set, the author reformulated the GSIP in [107] to an SIP through a linear variable transformation according to [86, 173, 63], cf. Section 4.2.3, and implemented it in BOARPET. Incomplete measurement data can, at least, theoretically, now be processed using this implementation, though this has not been fully tested.

3.2 Comparison to DECHEMA DPP

Disclaimer: Contributions to this section: Tjalf Hoffmann performed the regression with Gauss-Newton (DPP) using the files selected by the author. The author analyzed the regression results and the weakness of Gauss-Newton, and wrote this section. The author would like to point out the work of Johannes-Robert
3.2 Comparison to DECHEMA DPP

Bruch [26] who demonstrates the consequences of said weakness for the process simulation, by means of flash simulations. These were carried out by Bruch using the files selected by the author, and based on an early version of this section, entitled “Notes on Comparison of BOARPET (DPP) to Gauss-Newton (DPP)” in [26]. It should be noted that the parameter values reported in this section are not recommended for further use, as these are most probably of inferior statistical significance and/or goodness of fit. Acknowledgment: The author would like to thank Ulrich Westhaus (DECHEMA) for sharing his experience on working with the DPP flash routine with her.

In the following, we investigate whether the fact that Gauss-Newton (GN) through DECHEMA DPP implements only necessary (as opposed to sufficient) criteria for thermodynamic stability can affect the regression in practice, and if so, whether BOARPET through DECHEMA DPP allows for any improvements. The case studies at hand are binary LLE mixtures with an upper critical solution temperature (UCST) and/or a lower critical solution temperature (LCST). From experiments, it is evident that the systems exhibit only one phase split and the author is not aware of any binary system that would show more. It should be noted that the regression problems are challenging, as the objective function is highly nonlinear and potentially nonsmooth with respect to the parameters, while GN and BARON [161] rely on methods for smooth optimization problems.

3.2.1 Background on DECHEMA DPP

DECHEMA Data Preparation Package (DPP) [1] implements the regression of multicomponent fluid system data to thermodynamic models in phase equilibria. It uses proprietary implementations based on the methods in [117] in combination with routines from the prior DETHERM-SDC (DETherm Stoffdatencompiler) [5]. In particular, DPP seems to be conceptualized as follows: For each iteration of the regression algorithm operating in the parameter space, a flash routine is called, in order to determine the mole fractions that correspond to the parameter values of the current iteration. The flash routine searches for a feed composition which allows for a phase split, on a grid of 10 equidistant nodes in the mole fraction range (0,1), and upon success, calculates the corresponding equilibrium compositions [117, p. 78]. Both the temperature, the composition and/or the pressure may be regressed, leading to a so-called errors-in-variables model as opposed to a fixed-regressor model, e.g., [115]. Therefore, this flash procedure is applied over a temperature range in order to obtain the binodal curve from which the equilibrium compositions are then calculated using isoactivity. In the next iteration of the regression algorithm, the discrepancy between these calculated and the measured compositions is minimized by varying the parameter values, probably based on an orthogonal distance regression, and the loop is closed.

From the above described procedure, the flash routine most likely delineates the crucial part: The fact that a phase split occurs is established by checking for local concavity of the Gibbs free energy in mole fraction on the aforementioned grid [117]. In case local concavity is detected, the phase compositions in equilibrium are calculated from isoactivity (2.7) which is only a necessary but not sufficient criterion for thermodynamic stability; this system of nonlinear equations is solved by Newton’s method [117, p. 79]. Overall, this approach is nonrigorous, as the obtained compositions are not guaranteed to be global minimizers of the Gibbs free energy. Consequently, the results depend on initialization and specific initialization schemes are required [117, p. 80f.].

Finally, in DPP, there seem to be local checks for stability which rely on the second-order
derivative of the Gibbs free energy with respect to mole fraction at the predicted compositions [117, p. 173]. These are directly related to the KKT second-order sufficient optimality conditions (2.9) and, as such, only necessary but not sufficient for thermodynamic stability. On the other hand, in terms of optimization algorithms operating in the parameter space, DPP offers, e.g., the Nelder-Mead method, the Levenberg-Marquardt method, and a modified version of the Gauss-Newton (GN) method. On default for a binary LLE, GN is used in DPP. The original GN routine implements a line-search method based on Newton’s method, yet exploits the structure of the objective function by approximating the Hessian, cf. [115]. In contrast to GN (DPP), BOARPET (DPP) implements sufficient conditions for thermodynamic stability which suggest to interpret the parameter estimation problem either as a (G)SIP [107] or as a bilevel problem (2.10).

3.2.2 Computational Details

We use GN and BOARPET v1.4 [109], the latter calling GAMS 24.8, through DECHEMA DPP [1] 2016.0, build 1661, with dongle-license version 3600. Both GN and BOARPET complete the case studies with status “converged”. We use default DPP option settings, except we set $x_{\text{onepslo}}$, $x_{\text{onepsup}}$, in order to impose criteria sufficient for thermodynamic stability. We use the same parameter configurations, bounds and initials in both methods, cf. Tables C.1 and D.1, and the same measurement data. It should be noted that BOARPET stand-alone uses a temperature dependency of the regressed parameters based on the relative temperature $T_{\text{sc}}$. This allows good scaling of the parameter values and thus, facilitates determining tighter bounds as appropriate for global optimization [107]. This modified model reads

\[
\tau_{ij,\text{mtm}}(T) = A_{ij,\text{mtm}} + B_{ij,\text{mtm}} \left( \frac{T}{T_{\text{sc}}} - \text{tran} \right) + C_{ij,\text{mtm}} \left( \frac{T}{T_{\text{sc}}} - \text{tran} \right) + D_{ij,\text{mtm}} \cdot \ln \left( \frac{T}{T_{\text{sc}}} \right), \alpha_{12,\text{mtm}}(T) = E_{12} + F_{12,\text{mtm}} \left( \frac{T}{T_{\text{sc}}} - \text{tran} \right),
\]

also see Equation (3.7), whereas for models in IKC, DPP, or Aspen, $\tau_{ij,\text{ikc}}(T) = A_{ij,\text{ikc}} + \frac{B_{ij,\text{ikc}}}{T} + C_{ij,\text{ikc}} \cdot \ln (T) + D_{ij,\text{ikc}} \cdot T$ and

\[
\alpha_{12,\text{ikc}}(T) = \hat{\alpha}_{12,\text{ikc}} + \beta_{12,\text{ikc}} (T - 273.15).
\]

The calculations are run on a 64-bit processor 3.30 GHz Windows 7 Enterprise, Service Pack 1.

3.2.3 Case Study: THF/Water

This fluid system is challenging for parameter estimation, as it exhibits both UCST and LCST; we repeat the regression in [108] who use an early stand-alone version of BOARPET. The parameter values reported in Table C.1 are obtained with GN (DPP) and BOARPET (DPP), respectively. Figure 3.1 reveals that the parameter values found by GN give a spurious phase split at 373.15 K since $\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{ij}} < 0$, for $x_{ij} \in (0,1)\setminus[0.08831, 0.3968]$. As the spurious phase split (for $x_{\text{THF}} < 0.4$) is more pronounced than the true split (for $x_{\text{THF}} < 0.4$), the density of said grid on which the check is carried out can probably be excluded as the root of the problem. Altogether, this example demonstrates that a good fit with GN may come at the cost of a constraint violation in Problem (2.10), whereas BOARPET achieves a good fit (optimal objective function value $LS^* = 0.000108$, also see Equation (3.8)), guaranteeing thermodynamic stability.
3.2 Comparison to DECHEMA DPP

Fig. 3.1: Reduced Gibbs free energy of mixing as a function of mole fraction $x$ at 373.15 K, for the LLE of THF/water. Top and center: Parameter values reported by GN (DPP), cf. Table C.1, zoomed out and in, respectively, imply a spurious phase split. Bottom: Parameter values reported by BOARPET (DPP), cf. Table C.1, correctly imply a single phase split. BOARPET also returns the predicted mole fractions (0.3968, 0.0883) which allows for adding the respective tangent.
3 Parameter Estimation of Activity Coefficient Models in Nonreactive Systems

3.2.4 Case Study: Butanole/Water

This is a prominent fluid system example often used to test regression methods, partially due to the fact that it exhibits an UCST. For instance, [117, p. 80] demonstrate the capabilities of their flash routine by means of this very system. We use the measurement data from [137] and obtain the parameter values reported in Table D.1 with GN and BOARPET, respectively. Similar to THF/water, cf. Section 3.2.3, Figure 3.2 reveals a spurious phase split for the results of GN; for instance, at 371.85 K, $\left(\frac{\partial^2 \Delta G}{\partial x^2}\right)_{x_{i,j}} < 0$, for $x_{i,j} \in (0,1)\backslash[0.02016,0.2857]$. It should be noted that the initial point, cf. Table D.1, is chosen such that it represents a (local) minimum of Problem (2.10) without (2.10d). This is the unconstrained parameter estimation problem, in the sense that no constraints to prevent spurious phase splits are imposed. Since GN does not detect the pertinent constraint violation, the solver attaches to the initial point, while BOARPET correctly moves to a bilevel-feasible point of Problem (2.10).

3.2.5 Interim Conclusions

Two fluid systems known to be demanding for their occurrence of UCST and/or LCST are examined by means of the regression methods modified-GN calling the flash routine in [117], and BOARPET, both through DECHEM A DPP. The limited amount of examples allows to draw only some interim conclusions. For both THF/water and butanole/water, the results of GN, a method prevalent for parameter estimation [115], reported in this section, are not recommended for further use due to qualitative incorrectness. In particular, the parameter values reported by GN imply a spurious phase split, cf. Figure 2.1d. This is unexpected, as the method in [117] includes interim checks for local concavity of the Gibbs free energy, cf. Section 3.2.1, which can be easily adapted, in order to detect those splits. Interestingly, the spurious splits seem to occur at higher mole fraction values, suggesting that either the check for spurious phase splits is performed but this is not translated correctly to the return status of GN, or that said grid on which the check is carried out is not fully covered. In particular, the results seem to suggest that the check loops from a mole fraction value close to zero and terminates upon detection of the first (in these cases true) split. In our opinion, the change in implementation required to prevent this behavior is rather straightforward, in particular, a routine that loops over the mole fraction grid and terminates at a mole fraction value of unity, or/and looping in both decreasing and increasing direction over the mole fraction grid. It should be noted that using different initial values and bounds for the parameters, as well as nondefault option settings, with GN, a different result might have been obtained, in the sense of a different goodness of fit and most importantly, also in the sense of satisfying thermodynamic constraints, yet no such guarantees are offered by the method.

A feedback from the flash in the composition space to the regression in the parameter space would be desirable with GN (DPP), in order to avoid the observed constraint violations of Problem (2.10). The reason for this is that these demonstrably lead to considerable errors in, e.g., flowsheet calculations [26]. In contrast, the results from BOARPET are applicable since they satisfy Problem (2.10d). In the mathematical context of Chapter 2 this implies that only BOARPET returns a solution $(\mathbf{x}^u,\mathbf{q}^u)$ of Problem (2.10) which provides the desirable guarantee that a reliable UO model correctly regain $\mathbf{x}^u$ upon use of $\mathbf{q}^u$. 

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3.2 Comparison to DECHHEMA DPP

Fig. 3.2: Reduced Gibbs free energy of mixing as a function of mole fraction \( x \) at 371.85 K, for the LLE of butanole/water. Top and center: Parameter values reported by GN (DPP), cf. Table D.1, zoomed out and in, respectively, imply a spurious phase split. Bottom: Parameter values reported by BOARPET (DPP), cf. Table D.1, correctly imply a single phase split. BOARPET also returns the predicted mole fractions (0.2857, 0.02016) which allows for adding the respective tangent.
Finally, Equation (2.9) is satisfied at the predicted phases throughout, by GN (DPP) which is not always the case in other established tools, cf. Section 3.3. As a future step, it would be interesting to investigate the performance of the remaining regression solvers in DPP, and whether these interact similarly with the DPP flash routine [117]. Another issue would be the performance of the flash routine when multiple double-tangents occur within the same phase split, as the flash relies on isopotential only.

### 3.3 Comparison to Aspen DRS

**Disclaimer:** This section adopts the abstract and the sections entitled “Introduction”, “Parameter Estimation” and “Conclusions” from [59], which are also briefly summarized in [6]. Contributions to [59] and [6]: Maximilian Aigner performed the measurements for the specified temperature range, set up the sheet for parameter estimation in Aspen, and generated Figure 3.4 and Table E.1 also used in this thesis. The author performed the parameter estimation in both Aspen and BOARPET stand-alone, discovered the weakness of Aspen and formulated the optimization problem, in order to give a formal explanation for this weakness. Some typographical errors in the Appendices in [59] are corrected in this thesis. Furthermore, after [59] had been published, the regression was repeated, based on all of the measurement data that were available at that time, in [26]. For a higher statistical significance, the author recommends to use the parameter values reported in [26]. Acknowledgment: The author would like to thank Ralf Hannemann-Tamás for giving helpful advice on discussing the mathematical proof given in Appendix E.2.2.

State-of-the-art is fitting of phase equilibria models to measurement data, subject to thermodynamic stability. As this can result in a bilevel problem (2.10) it is challenging and requires dedicated algorithms, see [108, 107, 20]. While such a problem formulation is implemented in BOARPET [109], it is not in established tools, e.g., [8, 1], and [4, 120]. For the last decades, Aspen DRS, DEHEMA DPP, DDBSP and other regression tools have been substantially contributing to research progress in chemical engineering and related fields, by generating parameter sets for demanding fluid systems. In this chapter, we select Aspen DRS as a representative for the conventional parameter estimation, as it often is used in connection with the world’s leading process simulator, Aspen Plus [7]. We fit the NRTL model to LLE measurement data of the system 2MTHF/water between 293.15 K and 423.15 K, on the one hand with Aspen DRS, and on the other with the regression tool BOARPET. As opposed to regression results in the open literature [92, 158], the regressed temperature range is particularly broad which increases the statistical significance of the parameters obtained.

We would like to sensitize the reader to a weakness that we discovered in Aspen DRS, and that arises because the aforementioned bilevel formulation is not implemented in Aspen DRS. Furthermore, we would like to demonstrate how to easily check for this weakness, as there are no automatic warning and error messages. The purpose of Sections 3.3.1 and 3.3.3 is to investigate whether Aspen DRS yields results that satisfy thermodynamic stability. In particular, we examine the Gibbs free energy at the predicted composition of the 2MTHF-phase since local convexity of the Gibbs free energy is a necessary criterion for thermodynamic stability. In Appendix E.2, we formulate the KKT first- and second-order conditions for the minimization of the Gibbs free energy, subject to mass balance. In particular, we examine the possibility of the optimizer being misled by a saddle point since such a point satisfies the KKT first-order conditions for minimization.
3.3 Thermodynamic Stability

First, we state the optimization problem under consideration of the specific case of two phases and two species. For the general case, the problem statement is given in Appendix E.2.1. Let $p_h \in \{I, II\}$ denote the phases, $i \in \{1, 2\}$ the species, and 0 the feed. Let further $x_{i,ph}$ be the mole fraction, $\Phi$ the phase fraction, $\Delta \mu_{i,ph}$ the chemical potential relative to the reference state “pure, real liquid”, and $\Delta G$ the molar Gibbs free energy of mixing. In order to eliminate some variables without loss of generality, we directly use Equations (E.1b) and (E.1c). Consequently, the problem reduces to

$$\min_{\Phi, x_{1,I}, x_{1,II}} \Phi \Delta G(x_{1,I}) + (1 - \Phi) \Delta G(x_{1,II})$$

s.t. $x_{1,I} \Phi + x_{1,II}(1 - \Phi) - x^0 = 0$, \hspace{1cm} (3.2)

where $\Phi \in [0, 1], x_{1,I} \in [0, 1], x_{1,II} \in [0, 1]$ are scalars. The Lagrangian of this optimization problem is given by

$$L(\lambda, \Phi, x_{1,I}, x_{1,II}) = \Phi \Delta G(x_{1,I}) + (1 - \Phi) \Delta G(x_{1,II})$$

$$+ \lambda(x_{1,I} \Phi + x_{1,II}(1 - \Phi) - x^0),$$ \hspace{1cm} (3.3)

where $\lambda \in \mathbb{R}$ is the Lagrangian multiplier. In Appendix E.2.2, we postulate the KKT first-order conditions for a (strict) local minimum, excluding $\Phi \in \{0, 1\}$, i.e., the trivial case of single-phase solutions. We conclude that a point that satisfies isopotential,

$$\Delta \mu_{1,I}(x_{1,I}) = \Delta \mu_{1,II}(x_{1,II})$$

$$\Delta \mu_{2,I}(x_{1,I}) = \Delta \mu_{2,II}(x_{1,II}),$$ \hspace{1cm} (2.7)

the secant

$$\Delta \mu_{2,I}(x_{1,I}) - \Delta \mu_{1,I}(x_{1,I}) = \frac{\Delta G(x_{1,I}) - \Delta G(x_{1,II})}{x_{1,I} - x_{1,II}},$$ \hspace{1cm} (3.5)

and mass balance also satisfies the KKT first-order conditions and is a stationary point. Further, we derive the KKT second-order sufficient conditions for a (strict) local minimum. In particular, by Theorem 3

$$\left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,I}} \neq 0$$

$$\left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} \neq 0$$

$$\text{sign} \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,I}} = -\text{sign} \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}}$$ \hspace{1cm} (3.6)

in addition to the stationarity conditions is a sufficient, yet not a necessary criterion for the existence of a saddle point. In other words, strict local convexity and concavity of the Gibbs free energy at the predicted phase compositions $x_{1,I}$ and $x_{1,II}$, respectively, are sufficient for a saddle; these findings will be used in Section 3.3.3.
3.3.2 Computational Details

We use a 64-bit xenon processor 2.60 GHz running Windows 2008 R2 data center. For regression in Aspen DRS, the settings are: objective function “Maximum Likelihood”, algorithm “Britt-Luecke”, initialization method “Deming”, convergence tolerance 0.0001, standard deviation 0.655 % for mole fractions of organic phase measured using chromatography, standard deviation 0.1 % for all remaining mole fractions, standard deviation 0.01 K for all temperatures, “Test stability of LLE results” true. In our opinion, these settings represent well the choice of a typical user of commercial tools. In order to investigate the Gibbs free energy for the reported parameters, we generate a table of values $\Delta G(x)$ using the data analysis tool within Aspen DRS.

For the simulation in Aspen Plus, we use the built-in model RGibbs. The settings are: “maximum number of fluid phases” 2, “valid phases” vapor-liquid-liquid, “calculate phase equilibrium only” true, “vapor fraction” 0, “temperature” 423.176 K.

The implementation of BOARPET [109] is based on [108, 107, 20]. We use the global solver BARON [161] with the following settings: $AbsConFeasTol = 1e^{-7}$, $NlpSol = -1$, $LpSol = 3$, $BoxTol = 1e^{-5}$, $FirstFeas = 0$, $NumLoc = -2$, and parameters are prioritized over mole fractions. As opposed to the formulation implemented in Aspen DRS, BOARPET guarantees thermodynamic stability by using Baker’s criterion [12] in addition to the isopotential equation. It should be noted that with BOARPET, we use only 5 parameters (instead of 7 in Aspen DRS), as this results in a very good fit. Furthermore, upon convergence of BARON, BOARPET guarantees a global minimum, i.e., the best-possible fit of the given model to the experimental data. The temperature dependencies of the regressed parameters are basically following Aspen and are given by

$$\tau_{ij}(T) = A_{ij} + B_{ij} \left( \frac{298.15 K}{T} \right) - 1 + C_{ij} \left( \frac{T}{298.15 K} - 1 \right) + D_{ij} \ln \left( \frac{T}{298.15 K} \right)$$

and

$$\alpha(T) = E_{12} + F_{12} \left( \frac{T}{298.15 K} - 1 \right).$$ (3.7)

In addition, in BOARPET, the temperature is not regressed but kept constant ($(P, T)$-flash). Further, let $k = 1, \ldots, L$ denote the experiments. The residual $r_{ph,k}$ at phase $ph$ and for experiment $k$, and the objective function $LS$ implemented in BOARPET then read

$$r_{ph,k} = x_{measured,1,ph,k} - x_{predicted,1,ph,k}$$

and

$$LS = \sum_{k=1}^{L} \sum_{ph=1}^{II} w_{ph} r_{ph,k}^2,$$ (3.8)

where $w_{ph}$ is a weight, and is set to 1 for the organic phase and to 10 for the aqueous phase. Furthermore, the squared sum of residuals is given by $res_{abs} = \sum_{k=1}^{L} \sum_{ph=1}^{II} r_{ph,k}^2$. We exclude systematic measurement errors and assume that NRTL is a valid model to describe the measurement data, i.e., the residuals are unbiased. Further, assuming the measurement error to be independent and normally distributed, it follows for the estimate of measurement standard deviation $s$, see e.g., [11] $s = \sqrt{\frac{res_{abs}}{DOF}}$, where the degree of freedom $DOF = n_{meas} - n_{param}$ is the difference between the number of observations $n_{meas}$ and the number of estimated parameters $n_{param}$. Finally, the relative squared sums are given by

$$res_{rel,1} = \sum_{k=1}^{L} \sum_{ph=1}^{II} \left( \frac{r_{ph,k}}{x_{measured,1,ph,k}} \right)^2$$

and

$$res_{rel,2} = \sum_{k=1}^{L} \sum_{ph=1}^{II} \left( \frac{r_{ph,k}}{x_{predicted,1,ph,k}} \right)^2.$$
3.3 Comparison to Aspen DRS

3.3.3 Case Study: 2MTHF/Water in Aspen DRS

The NRTL model is fitted to measurement data (for measurement data, cf. Table E.1) of the LLE of the system 2MTHF/water between 293.15 K and 423.15 K using Aspen DRS [8]. In this section, we present the results of this regression. The initial values, bounds and regressed values are given in Table E.2, while the regressed values of temperature and composition in each phase are depicted in Table E.3. The correlation matrix and standard deviation with respect to the parameters are given in Appendix E.3. It should be noted that highly correlated parameters are partially due to parameter definitions according to the NRTL model, also see [8].

For the reported results of the regression, we check for the KKT first- and second-order conditions for the specific case of 423.176 K which is a temperature value predicted by Aspen DRS for the experiment at 423.15 K. For the phase compositions in equilibrium, Aspen DRS reports $x_{1,1} = 0.0118653$ and $x_{1,II} = 0.7859$. From the approximated phase compositions and tabulated $\Delta G(x)$, we approximate the first- and second-order derivatives by central finite differences, and also calculate the slope of the secant. Ideally, the secant and the tangent coincide, see Figure 3.3. In particular, we approximate the derivatives according to

$$\left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,ph}} \approx \frac{\Delta G(x_{1,ph} + 1/2\delta x) - \Delta G(x_{1,ph} - 1/2\delta x)}{\delta x},$$

$$\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,ph}} \approx \frac{\Delta G(x_{1,ph} + \delta x) - 2\Delta G(x_{1,ph}) + \Delta G(x_{1,ph} - \delta x)}{\delta x^2}. \quad (3.9)$$

It should be noted that the Gibbs free energy exhibits different curvatures at the phases, cf. Figure 3.3. Hence, $\delta x = 0.2e-4$ is appropriate for the aqueous phase but for the organic phase it would result in finite differences of 0, i.e., below the numerical accuracy of Aspen. On the other hand, $\delta x = 0.2e-2$ is appropriate for the organic phase but it would result in an inferior approximation at the aqueous phase. Consequently, we use different finite differences $\delta x$ for each phase. The numerical values for the slope of the secant, as well as the approximated first- and second-order derivatives are given in Table 3.1. Table 3.1 shows that Aspen DRS meets isopotential, cf. Equation (2.7), within a tolerance of less than 2.1 %, and the slope of the secant meets the slope of the tangents, cf. Equation (3.5), within a tolerance of less than 1.8 %. We conclude that Aspen DRS satisfies the KKT first-order conditions satisfactorily, and hence, identifies a stationary point of the optimization problem, within a tolerance of about 2.1 %. It should be noted that this error is partly due to approximating the derivatives by finite differences. Since $\left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,1}} < 0$ and $\left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,II}} > 0$ as shown in Table 3.1 and Figure 3.3, by Theorem 3 Aspen DRS finds a saddle point of Equation (3.3), while it should find a minimum, and thus, thermodynamic stability is violated even locally. Presumably, the optimizer is misled by a saddle point trying to minimize the Gibbs free energy, because the saddle point of Equation (3.3) satisfies the stationarity conditions. This can be avoided by imposing the constraints $\left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,1}} \geq 0$ and $\left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,II}} \geq 0$ during the regression, also see [94] which we consider to be straightforward in terms of implementation. We would like to point out that, however, even these are only necessary but not sufficient criteria for thermodynamic stability.

Until Aspen DRS implements such a check the author would like to encourage the reader
Table 3.1: First- and second-order derivatives approximated by central finite differences, and the slope of the secant for the regression using Aspen DRS [8]. The phase compositions that Aspen DRS reports at 423.176 K are approximated: \( x_{1,1} = 0.0118653 \approx 0.01187 \) and \( x_{1,II} = 0.7859 \approx 0.786 \).

<table>
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<th>( x_{i,ph} )</th>
<th>( \Delta G )</th>
<th>( \frac{\partial^2 \Delta G}{\partial x^2} )</th>
<th>( \frac{\partial \Delta G}{\partial x} )</th>
<th>( \Delta G(x_{i,ph}) - \Delta G(x_{i,ph+1}) )</th>
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Fig. 3.3: Molar Gibbs free energy of mixing \( \Delta G \) in J kmol\(^{-1}\) as a function of composition in mol mol\(^{-1}\) at 423.176 K. Plain plot generated by Aspen DRS [8]. Continuous and dashed tangent and vertical lines to indicate phase compositions are added. Continuous tangent: Aspen DRS reports \( x_{1,1} = 0.0118653 \) and \( x_{1,II} = 0.7859 \) for the phase compositions. At \( x_{1,II} \), the Gibbs free energy is locally concave which violates thermodynamic stability even locally. Dashed tangent: Thermodynamic stability is satisfied globally. While \( x_{1,1} \) is not significantly changed, \( x_{1,II} \approx 0.9381 \neq 0.7859 \) would give different flash results than what the regression assumes.
Fig. 3.4: LLE data for the system 2MTHF/water in the temperature range from 273.15 K to 423.15 K. Red circles: gas chromatography analysis data, blue triangles: spectroscopic data, solid curve: model prediction. It should be noted that only the data from [59] are used for regression.

to follow this simple check for the applicability of the reported parameter values. Should thermodynamic stability be violated, there is a chance of satisfying it by manipulating the initial parameter values by trial-and-error. Alternatively, our regression tool BOARPET can be used that considers thermodynamic stability during the fitting and thus, stability is guaranteed.

3.3.4 Case Study: 2MTHF/Water in BOARPET

The NRTL model is fitted to measurement data (for measurement data, cf. Table E.1) of the LLE of the system 2MTHF/water between 293.15 K and 423.15 K using our regression tool BOARPET [109]. In this section, we present the results of this regression; we determine the parameters given in Table E.5 which are valid for the temperature range $293.15 \text{ K} \leq T \leq 423.15 \text{ K}$. We obtain an objective function value $LS = 0.29517 \cdot 10^{-2}$, an estimate of measurement standard deviation $s = 0.10646 \cdot 10^{-1}$, a squared sum of residuals $res_{abs} = 0.21536 \cdot 10^{-2}$, and relative squared sums $res_{rel,1} = 0.79438$ and $res_{rel,2} = 0.42252$ which demonstrate the good agreement between the fitted model and the experiments, also see Figure 3.4. Implementing the calculation of these and additional basic statistical data in BOARPET is left for future work. Finally, the regressed values of temperature and composition in each phase are given in Table E.4. Comparing Table E.5 to Table E.2 it is conspicuous that with BOARPET, only 5 parameters are required, and the parameter values are in a more practicable range. In terms of CPU time, the fitting in Aspen DRS takes a couple of seconds whereas with BOARPET, the CPU time is around 25 min. Comparing now Figure 3.5 to Figure 3.3 with respect to Baker’s criterion, it can be shown that BOARPET yields parameter values guaranteeing thermodynamic stability globally, while Aspen DRS provides parameter values that violate stability even locally.
Fig. 3.5: Reduced molar Gibbs free energy of mixing as a function of mole fraction $x$ at 423.15 K. BOARPET [109] reports $x_{1,I} = 0.0068679$ and $x_{1,II} = 0.78204$ for the phase compositions. Thermodynamic stability is satisfied globally. For instance, the reduced Gibbs free energy is locally convex at both $x_{1,I}$ and $x_{1,II}$.

Let us now take the very common case of a ($P,T$)-flash calculation, e.g., in the course of a process simulation, using the parameter values generated by Aspen DRS. A flash problem that is solved to global optimality of the Gibbs free energy will then result in the phase compositions that can be obtained using the dashed tangent in Figure 3.3 according to Baker’s criterion. In Aspen Plus, a flash simulation using RGibbs results in the phase compositions $x_{1,I} \approx 0.01175$ and $x_{1,II} \approx 0.9381$, and the latter is significantly different from what regression assumes. In contrast, a flash problem that is solved using the parameter values of BOARPET will give the correct phase compositions since the flash problem will correctly result in the same tangent as the model fitting, cf. Figure 3.5. It should be noted that in this specific case even local optimization would give the same (correct) phase compositions; in general terms, however, flash problems need to be solved to the global optimum of the Gibbs free energy. ([111] demonstrate the consequences of using incorrect parameter values in dynamic distillation models, subject to such a global flash.) It should be noted further that BOARPET finds very good fits provided these are possible by the model, as it uses global optimization. Besides a good fit, the focus of this work is predominantly on thermodynamic stability, as this is an unconditional prerequisite for the applicability of the parameter values.

### 3.3.5 Interim Conclusions

The NRTL model is fitted to experimental data for the LLE of 2MTHF/water, in both Aspen DRS and the regression tool BOARPET. While BOARPET solves Problem (2.10) that guarantees thermodynamic stability, it is found that the results of Aspen DRS reports an infeasible point of Problem (2.10). Furthermore, the results violate thermodynamic sta-
bility even locally, i.e., the KKT second-order sufficient conditions (4.6d). We investigate the problem formulation of the minimization of the Gibbs free energy and find that Aspen’s optimizer presumably is misled by a saddle point, because this point satisfies the stationarity conditions. This gives a hitherto unknown motivation to use a rigorous problem formulation in parameter estimation. Conventional problem formulations implemented in established tools, such as Aspen DRS, may provide parameter values that are not applicable. We would like to sensitize the reader to this weakness, as it is of methodological nature and is, thus, not restricted to the fluid system under consideration, nor the NRTL model.

3.4 Case Study: 3MTHF/Water

Disclaimer: This section adopts the section entitled “Data Regression of LLE 3-MTHF/Water” from [88]. Contributions to said submitted supplement: Dominik Limper performed the measurements, resulting in the measurement data reported in Tables 5 to 7 in [88]. The author complemented the measurement data with those from the literature, and performed the regression in BOARPET.

In this section and Appendix F, we document the complete collection of measurement data that are currently available, and give parameter values of the NRTL model, for the LLE of the binary fluid system 3MTHF/water. To our best knowledge, [88] are the first to report i) a model for this phase equilibrium, and ii) all of the measurement data. The measurement data are taken from [37, 25, 88, 16], and are assembled in Tables F.1 to F.3. For the data in [88], the temperature is not measured but assumed to be ambient temperature, i.e., 25°C. It should be noted that some of the data are not used due to discrepancy with the majority of the data. Furthermore, [88] provide data for the single-phase system and the azeotrope which are not used since they are deemed less informative, or are incomplete, cf. Table F.2.

The parameters are generated using the regression tool BOARPET [109] which is based on [108, 107, 20]; the regressed values are reported in Table F.5. We use the temperature dependency of the regressed parameters given by Equation (3.7) and an objective function according to Equation (3.8), where \( w_{ph} = 1 \) for the organic phase and \( w_{ph} = 10 \) for the aqueous phase. The regression results in a good fit (optimal objective function value \( LS^* = 0.0292 \)), cf. Figure 3.6, and also correctly reflects single-phase states where the measurement data in [88] suggest, cf. Table F.3.

3.5 Water/Platform Molecule Mixtures

Disclaimer: This section adopts almost the entire content from the poster entitled “Modeling Miscibility Gaps in Water/Platform Molecule Binary Mixtures” of the author, Johannes-Robert Bruch, Jörn Viell and Alexander Mitsos, presented at the 5th International Conference of the Cluster of Excellence Tailor-Made Fuels from Biomass (TMFB) in Aachen. Contributions to the poster: Johannes-Robert Bruch performed the NRTL parameter estimation with BOARPET for 2MTHF, 2,5DMTHF, 2,5DMF and 2MF and generated all of the data in Figure 3.7 [26]. For these, he used the measurement data from [38]. The author performed the parameter estimation for 3MTHF [88], also see Section 3.4, developed the criterion for the purity thresholds with the help of Jörn Viell, and finally calculated the purities, compared the
Fig. 3.6: Temperature $T$ with respect to mole fraction $x$ of 3MTHF of the LLE of 3MTHF/water. Black curves: model predictions, filled red squares: measurements from [37], filled red triangles: measurements from [25], filled red circles: measurements from [16], plain blue circles: measurements from [88]. For the sake of completeness, we also report plain blue triangles: single-phase and plain blue square: azeotropic measurements from [88].

miscibility gaps and drew the conclusions on fuel and solvent potentials.

When converting biomass to platform molecules and biofuels, LLE are likely to occur. As opposed to measurement data only, an appropriate (LLE-)model allows to integrate fuel design, reaction network flux analysis (RNFA, [170]), fuel/platform molecule synthesis and basic process concepts with automated process design. Thus, these models allow to assess the potential of a molecule as ready-to-use fuel or solvent and to facilitate molecule tailoring by means of candidates screening. For said assessment, in general terms, wide miscibility gaps are deemed advantageous due to higher purities of the phases formed. In particular, we assume the following thresholds:

- Assumed solvent requirement: sufficient purity (threshold 99 wt% H$_2$O at 298 K) of the aqueous phase. This allows for low recycles, while no cooling/heating is required in the biorefinery process.

- Assumed ready-to-use fuel requirement: sufficient purity (threshold 99 wt% organic species at 298 K) of the organic phase. For fuel candidates, 298 K is the assumed tank temperature.

[26] calculates NRTL parameters with BOARPET that correctly capture the LLE of water/platform molecule binary systems. A selection of the resulting model predictions is presented in Figure 3.7. We use the models to calculate purities of all phases at any relevant temperature given in Tables 3.2 and 3.3. Since both of the MF-derivatives, 2-methylfuran (2MF) and 2,5-dimethylfuran (2,5DMF) meet the purity thresholds for the organic and aqueous phase, we consider them potential ready-to-use fuels and solvents.
3.5 Water/Platform Molecule Mixtures

Fig. 3.7: Temperature $T$ with respect to mole fraction $x$ of tetrahydrofuran-derivatives of the LLE of each organic species with water. Solid curves: 3MTHF, dashed curves: 2MTHF, dash-dotted curves: 2,5DMTHF, dotted line: assumed tank/ambient temperature. Data plotted from [26].

Table 3.2: Separation efforts and, based on purity, the potential as solvent and/or ready-to-use fuel, for MF-derivatives. Assumed tank temperature is 298 K.

<table>
<thead>
<tr>
<th>Model predictions</th>
<th>2MF</th>
<th>2,5DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity aq. phase</td>
<td>99.1 wt% H$_2$O</td>
<td>99.6 wt% H$_2$O</td>
</tr>
<tr>
<td>Purity org. phase</td>
<td>99.8 wt% 2MF</td>
<td>99.9 wt% 2,5DMF</td>
</tr>
<tr>
<td>Separation effort</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Potential</td>
<td>Ready-to-use fuel/solvent</td>
<td>Ready-to-use fuel/solvent</td>
</tr>
</tbody>
</table>

Table 3.3: Separation efforts and, based on purity, the potential as solvent and/or ready-to-use fuel, for THF-derivatives. Assumed tank/ambient temperature is 298 K.

<table>
<thead>
<tr>
<th>Model predictions</th>
<th>2,5DMTHF</th>
<th>2MTHF</th>
<th>3MTHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity aq. phase</td>
<td>95.0 wt% H$_2$O</td>
<td>88.0 wt% H$_2$O</td>
<td>87.7 wt% H$_2$O</td>
</tr>
<tr>
<td>Purity org. phase</td>
<td>98.0 wt% 2,5DMTHF</td>
<td>96.2 wt% 2MTHF</td>
<td>95.2 wt% 3MTHF</td>
</tr>
<tr>
<td>Separation effort</td>
<td>Higher</td>
<td>Higher</td>
<td>Higher</td>
</tr>
<tr>
<td>Potential</td>
<td>Ready-to-use fuel/solvent</td>
<td>Solvent</td>
<td>Solvent</td>
</tr>
</tbody>
</table>
with low separation effort. At an assumed tank temperature of 298 K, a decanter would be sufficient for a separation. In contrast, none of the THF-derivatives satisfies these purity thresholds within the temperature range that we consider. Due to the temperature dependency of the miscibility gap, at 356 K, a purity of 98.7 wt% water can be achieved for 2,5-dimethyltetrahydrofuran (2,5DMTHF) in the aqueous phase. Similarly, for 2MTHF, up to 97.5 wt% water at 423 K and for 3MTHF, up to 88.6 wt% water at 323 K are reasonable. Therefore, THF-derivatives can be considered potential solvents only with significantly higher separation efforts since, e.g., rectification membrane techniques are required.

To conclude, the effects of functional groups in organic species, among others, come into play when assessing biofuel and solvent candidates. This can eventually pave the path to automated process design. Further considerations should extend these assessments based on the purities of the phases to specific costs and life-cycle analyses.
Data regression for reactive systems often is employed in connection with the Gibbs free energy models of electrolyte systems and thus, plays an important role in water treatment, electrolysis and the chemical industry. For the process simulation and optimization by means of these models, thermodynamically accurate model parameters are indispensable. Therefore, a lot of academic research has been addressing parameter estimation in thermodynamics, e.g., [35, 53, 152, 159]. In the chemical industry, the most prevalent methods for regression involved with the Gibbs free energy models arguably are those implemented in [8, 3, 45], also see [120]. By regressing data for demanding fluid systems, these tools have been contributing considerably to progress in the field of chemical engineering for years. The tools follow a method which casts the regression problem as a minimization of the model-experiment mismatch, subject to necessary (as opposed to necessary and sufficient) criteria for thermodynamic stability, or rely on black-box calls to flash algorithms.

Regression techniques similar to the aforementioned implementations can be found in the literature. For instance, [15] regress binary interaction parameters of the electrolyte universal quasichemical functional group activity coefficients (UNIFAC) and Pitzer-Debye-Hückel model [132, 133] using least-square errors. The chemical reaction equilibrium is described by means of the equilibrium constant which gives a criterion that is only necessary but not sufficient for thermodynamic stability, cf. Equation (2.8). [21] revise the eNRTL model in [30] with respect to thermodynamic consistency. They conduct a fit of the VLE of sulfuoric acid/water, considering partial dissociation and stepwise deprotonation, subject to the same necessary criterion for thermodynamic stability as [15]. Further, [21] mention the regression subject to the minimization of the Gibbs free energy and with regards to this, classify the regression problem as a demanding program. As a follow-up, [138] present the fitting of the eNRTL model to various experimental data of the same fluid system, constituting four coupled chemical reactions. Similar to [15] and [21], the residual root mean-square error is minimized, subject to the chemical reaction equilibrium constant.

There are also several attempts to consider thermodynamic stability more rigorously when minimizing the model-experiment mismatch. For instance, [31] regress Pitzer’s model [132, 133] to VLE data of phosphoric acid/water. Most importantly, they seem to use an early bilevel approach, i.e., they use the solution of the nonconvex minimization of the
Gibbs free energy for the phase and chemical reaction equilibrium, in order to obtain the compositions required for regression. However, only local solvers are used and the termination of the proposed algorithm is not discussed. Similarly, [167, 168] fit multiphasic equilibrium data to the extended eNRTL model. For the phase and chemical reaction equilibrium, they solve a convex optimization problem. Convexity is obtained by assuming that the complicating terms are constant, i.e., composition independent [101]. As a consequence, at constant composition, the global minimum of the Gibbs free energy is attained with even local solvers. In an outer loop, the composition dependence is updated such that, upon convergence, the originally nonconvex problem is solved to global optimality and thus, sufficient stability conditions for the phase and chemical reaction equilibrium seem to be considered. Finally, we would also like to point out [152, 153, 151] in which, although only phase equilibrium is considered, the regression method shows significant advancements which can also be readily applied to the chemical reaction equilibrium. They fit the (e)NRTL model to LLE including ionic liquid systems. In particular, they use interval analysis. In a first step, they determine all of the stationary points of the minimization of the Gibbs free energy. In a second step, they exclude those points that violate stability or exhibit other undesired behavior of the Gibbs free energy, with mathematical guarantee. However, this approach is limited to particular configurations of the thermodynamic parameters.

In this chapter, we consider predominantly the stable chemical reaction equilibrium and only briefly discuss the phase equilibrium. From the aforementioned works, [31, 168] are probably closest to ours. In particular, we introduce a BLP formulation which accounts for criteria that are both necessary and sufficient for thermodynamic stability of reactive systems, including the correct number of phases, during the regression. These criteria constitute the original reactive tangent plane criterion (RTPC) [154] (and follow-ups [81, 80]). As main contributions of this chapter, we demonstrate severe issues with regression subject to the chemical reaction equilibrium constant and how this can lead to erroneous values for the extent-of-reaction at equilibrium, in process simulation. Furthermore, we extend [20, 107, 108] from the tangent plane criterion (TPC) of [12] to the RTPC, i.e., the problem formulation is expanded from phase equilibrium only to both phase equilibrium and chemical reaction equilibrium. In particular, said extensions concern the formulation and choice of the LLPs, an improved discretization scheme, and the determination of the Lagrangian multipliers, including a discussion of constraint qualifications (CQs). The latter are required for the LBP of the applied algorithm. In terms of bilevel algorithm, we will use the LBP from [110] as is done in [20, 107, 108].

We would like to emphasize that, at least for binary, multiphase systems with all species present in all of the phases, a simple conversion scheme can be derived to convert between the RTPC and the TPC. As an implication, the RTPC and TPC become interchangeable. However, a special application of the RTPC are single-phase reactive systems on which we will, thus, focus in this work. It should be noted that this work does not cover (extensively) the specific cases of reactions with constant total molar amount [80], vanishing and reappearing phases [70, 155], charged species [14], reactive azeotropes [13, 71], nor the limitation of reaction paths [147], which are each treated elsewhere (without a link to parameter estimation in the respective references), nor does it cover the case of species being absent in some of the phases.

This chapter is structured as follows: In Section 4.1, we discuss the RTPC and its reduction to necessary criteria. These constitute an important part of the BLP formulation, which is
4.1 Thermodynamic Stability in Reactive Systems

In this section, we discuss the fundamental thermodynamic criterion on which the formulation proposed in Section 4.2.1 is based, also see Section 2.1; this is thermodynamic stability in the form of the RTPC for the minimization of the Gibbs free energy of reactive systems. In general terms, this minimization problem can be formulated in two different variable spaces, following the so-called nonstoichiometric (constrained) and the stoichiometric (unconstrained) approach [103]; between these two a linear transformation holds [155], cf. Section 4.3.1. In the latter case, the atom balance constraint can be given in explicit form and can, thus, be eliminated resulting in an unconstrained problem. It is the nonstoichiometric approach which is used for the derivation of the tangent criterion (RTPC).

4.1.1 Reactive Tangent Plane Criterion (RTPC)

While [154] demonstrate that the TPC [12] is a special case of the RTPC, [81] show that, in turn, the RTPC and TPC each represent special cases of an even more general problem formulation. One of the multiple alternatives to formulate the RTPC is derived by [154] from Equation (2.4). For \( \lambda^*_{ij} \) satisfying Equation (2.3) the pertinent variant of the RTPC reads

\[
\sum_i x_{i,ph} \left( \mu_{i,ph}(x_{ph}, q) - \sum_j \lambda^*_{ij} A_{ji} \right) \geq 0, \quad \forall x_{i,ph} \in (0, 1),
\]

i.e., the KKT point be below or equal to the function \( \forall x_{i,ph} \in (0, 1) \) and be, thus, the global minimum. Most importantly, the RTPC is both sufficient and necessary for thermodynamic stability. In terms of a physical meaning, \( \lambda^*_{ij} \) may be interpreted as the so-called elemental potential, as it can be shown that it equals the first-order derivative of the Gibbs free energy with respect to the elemental composition of a phase [129, 154]. On the other hand, \( \lambda^*_{ij} \) also has a geometric meaning. [81, 80] show by means of Equation (2.3a) that it is related to the slope of a tangent to the Gibbs free energy. In particular, they derive a geometric interpretation of the RTPC as a generalization of [12], by exploiting the closure condition Equation (2.1c), in order to reduce the dimensionality of the space of species to \( N - 1 \), and by rearranging Equation (4.1) to

\[
G(x, q) - \Theta(\bar{x}) \geq 0, \quad \forall \bar{x} \in (0, 1)^{N-1}.
\]

It should be noted that the reduction to \( N - 1 \) can be a considerable advantage of the tangent criteria (RTPC;TPC) over the direct minimization of the Gibbs free energy cast
in a space of dimensionality \( N \) \cite{100}. In Equation (2.5), \( G(x, q) \) denotes the molar Gibbs free energy relative to some reference state of formation, and

\[
\Theta(x) := (\lambda^*)^T(Ax + c)
\]

(4.2)

the supporting hyperplane which we adopt; \( A \in \mathbb{R}^{MR \times (N-1)} \) and \( c \in \mathbb{R}^{MR \times 1} \) are calculated from \( A' = (a'_1, \ldots, a'_{N-1}) \) according to

\[
A = (a'_1 - a'_N, \ldots, a'_{N-1} - a'_N)
\]

(4.3)

\[
c = a'_N.
\]

(4.4)

Specifically for reactive systems, \cite{81} show that the interception of \( \Theta(x) \) with the abscissa according to Equation (4.2) is fixed (due to stoichiometry) and hence, for a variable slope, i.e., a variable Lagrangian multiplier \( \lambda \), the geometric criterion comprises a rotating tangent plane. Further, as an advantage of the RTPC over the TPC, a single-phase solution is generally nontrivial, as it allows to calculate, e.g., the extent-of-reaction at equilibrium. In terms of visualization of the global minimization of the Gibbs free energy of (non)reactive systems, this geometric interpretation is limited to low-dimensional applications, i.e., quaternary or ternary fluid systems maximum. In most reactive systems, however, the dimensionality of the mole fraction space, \( N - 1 \), is likely higher, especially in the case of multiple reactions in parallel.

### 4.1.2 Variation of the RTPC

\cite{81, 80} state that the number of points at which the reactive tangent plane coincides with the surface of the Gibbs free energy curve indicates the number of phases. Together with the formulation in \cite{107} for the TPC, we can derive from Equation (2.5) that

\[
G(\bar{x}, q) - \Theta(\bar{x}) > 0, \ \forall \bar{x} \in X,
\]

(4.5)

is a necessary and sufficient criterion for the absence of any points of tangency, i.e., phases on the set \( X \subseteq (0, 1)^{N-1} \). \( X \) is open in case \( Ph = 1 \) and closed if \( Ph \geq 2 \); the properties of \( X \) are specified in Section 4.2.3. It should be noted that Equation (4.5) is a semi-infinite constraint with a strict inequality.

### 4.2 Proposed Bilevel Program

In this section, we specify Problem (2.10) to the case of reactive systems. For the nonconvex LLPs, we consider \( i \) thermodynamic stability of the predicted mole fractions satisfying the RTPC (Equation (2.5)) and \( ii \) the same number of phases as observed in the experiments (Equation (4.5)).

#### 4.2.1 Problem Statement

A general structure of the BLP is given by Problem (4.6).

\[
\begin{align*}
\min_{x^n, \lambda^n, n^n, q^n} & \ f^n(x^n, \lambda^n, n^n, q^n) \\
& \text{subject to:} \\
& \text{Equation (4.5)}
\end{align*}
\]

(4.6a)
4.2 Proposed Bilevel Program

\[ \text{s.t. } h^{u,1}(x^u, \lambda^u, q^u) = 0 \]  
\[ h^{u,2}(x^u, n^u) = 0 \]  
\[ g^u(x^u, q^u) \leq 0 \]  
\[ -f^{l,lp}(x^{u,lp}, \lambda^u, q^u) \leq 0 \]  
\[ x^{u,lp} \in \arg\min f^{l,lp}(x^{l,lp}, \lambda^u, q^u) \]  
\[ x^{l,lp} \in LLP \]  
\[ \forall lp \in LLP \]  
\[ \text{s.t. } g^{l,lp}(x^u, x^{l,lp}) \leq 0 \]  
\[ x^{l,lp} \in X^{l,lp}, x^{u,lp} \in X^{u,lp}, x^u \in X^u, \lambda^u \in \Lambda^u, n^u \in N^u, q^u \in Q^u, \]

where \( \lambda^u \) denotes the Lagrange multipliers for the RTPC (Section 4.1.1). This is an extension of Problem (2.10) in the sense that \( n^u \) and \( \lambda^u \) are additional variables. They are required to capture the chemical reaction equilibrium in addition to the phase equilibrium. On the other hand, certain LLPs are deemed to be redundant, see the following section.

4.2.2 Lower-Level Problems

The RTPC (Equation (2.5)) and Equation (4.5) each represent a particular type of LLP, to be imposed at all data points \( k = \{1, \ldots, K\} \) as constraints on Problem (4.6). \( \lambda^u \) and \( q^u \) are communicated from the upper level to these LLPs.

In the case of the RTPC, \( g^{l,lp}(\cdot) \) is not imposed since the RTPC shall hold on the entire mole fraction range, cf. Equation (2.5). Further, the global minimizers of each LLP, \( x^{u,lp} \), are collected in \( x^u \) and communicated to the upper level which allows for the interpretation of the parameter estimation problem as a BLP. It should be noted that the RTPC is required as an LLP to ensure the fulfillment of thermodynamic stability.

In contrast, in the case of Equation (4.5), \( x^u \) coming from those LLPs that involve the RTPC, is required. It will impose \( g^{l,lp}(\cdot) \) on the pertinent lower level. The resulting objective function value \( f^{l,lp}(x^{u,lp,\ast}, \lambda^{u,\ast}, q^u) \) is communicated to the upper level which suggests to interpret the parameter estimation problem as a generalized semi-infinite program (GSIP); the reduction to an SIP is discussed in Section 4.2.3. It should be noted that this LLP is required to avoid the prediction of any spurious phases.

[107] propose an additional LLP that prevents the prediction of spurious phase splits (spurious tangent planes); for the chemical reaction equilibrium, this can be interpreted as the guarantee of the correct number of chemical reactions, i.e., the correct number of reactive tangent planes. From Equations (4.3) and (4.4), it follows that these rely solely on the reaction stoichiometry in the form of \( A^1 \) which is potentially nonunique for a given reactive system [155]. From inspection of the case of a single reaction invariant and two species, we obtain a unique reactive tangent plane for all of the variants of \( A^1 \) (interchanged species, interchanged reaction invariants). Therefore, we would like to conjecture that the nonuniqueness of \( A^1 \) will not affect the uniqueness of the reactive tangent plane; a mathematical proof is left for future work. As a result, the BLP does not need to be restricted with respect to spurious reactive tangents. Further, if the conjecture holds, this will be another advantage of the RTPC over the TPC.
4.2.3 Lower-Bounding Problem

By discretizing $X^{l,lp}$, Problem (4.6) may be relaxed to an NLP, furnishing a LBP for the bilevel algorithm in [110]. For both types of LLPs, this discretization is straightforward as will be shown in this section.

Let $\hat{X}^{l,lp} = \{\hat{z}_1^{l,lp}, \ldots, \hat{z}_D^{l,lp}\}$ denote such a discrete set comprising points $\hat{z}_d^{l,lp} \in (0, 1)$, and $\Delta$ and $\epsilon$ some tolerances to warrant $x_d^u \in (0, 1)$ and to apply the bilevel algorithm, respectively. Then, the lower-level variables can be expressed as functions of these discrete points according to

\[
\hat{x}_d^{l,lp} = \begin{cases} 
\epsilon + \hat{z}_d^{l,lp} (x_d^u - \Delta - \epsilon), & \text{if } g^{l,lp}(\cdot) = x^{l,lp} - x^u \\
\hat{z}_d^{l,lp}, & \text{if } g^{l,lp} \text{ is not imposed,}
\end{cases}
\]

where $x_d^u = x_{i,p}^u$ are the corresponding elements of the upper-level variable vector $x^u$. Therefore, only $\hat{z}_d^{l,lp}$ need to be discretized, exploiting the fact that their discretization is not subject to $g^{l,lp}(\cdot)$. Interpreting the parameter estimation problem as a GSIP [107], the simple linear form of $g^{l,lp}(\cdot)$ allows, thus, even the reduction to an SIP which is both numerically and algorithmically advantageous. For a different type of model, such a kind of reformulation is discussed by [86], based on [173], also see Section 3.1.

4.3 Illustrative Case Studies

For illustrative purposes, we consider the fictitious exothermic liquid-phase dimerization reaction

\[
Z_2(1) \rightleftharpoons 2 \text{Z}(2).
\]

Together with the choice of $Z$ (as a single reaction invariant) for the atom balance, from Equations (4.3) and (4.4), we obtain

\[
\Theta(x) = \lambda (x + 1)
\]

for the reactive tangent plane, cf. Equation (4.2) and thus, $x_0 = -1$ for the intercept with the abscissa in the following Figures 4.1 to 4.6.

4.3.1 Computational Details

We use a 64-bit processor 3.30 GHz running Windows 7; the problems are hard-coded and solved with the global solver BARON through GAMS 24.9.1 [161] with default option settings. The algorithm in [110] is applied in such a way that the LBP is solved employing BARON, while the LLPs are univariate so that the checks for their violation are performed by plotting the respective tangent plane to the Gibbs free energy curve. Therefore, in Section 4.3, we use figures, in order to visualize the LLPs and check for bilevel-feasibility of the points that are reported as solutions. For the optimality tolerances, we set optca and optcr each to 1e-4, and the time-out reslim to 120s. As a first Gibbs free energy model, Margules is used for the binary system, due to its simple structure and nonconvexity. It allows the demonstration of several issues with conventional formulations. The LBP sub-problems...
are reliably solved by BARON with default option values. As a second Gibbs model, we employ the NRTL model for it is well-known and often used in industry. The temperature dependency of the regressed parameters in the respective activity coefficients is incorporated in both cases. Altogether, the (dimensionless) parameters read \( \mathbf{q} = (A_0, A_1, B_0, B_1)^T \) and \( \mathbf{q} = (A_{12}, F_{12}, A_{21}, F_{21})^T \) for Margules and NRTL, respectively, in the BLP notation. In particular, for the two-constant Margules model, we use, 

\[
\frac{\mu}{RT}(x,T) = G_{f,01} + G_{f,02}(1-x) + x \ln(x) + (1-x) \ln(1-x) + x(1-x)(A(T) \cdot (1-x) + B(T) \cdot x), \quad \frac{\mu}{RT}(x,T) = G_{f,01} + \ln(x) + (1-x)^2(A(T) + 2x(B(T) - A(T))),
\]

\[
\frac{\mu}{RT}(x,T) = G_{f,02} + \ln(1-x) + x^2(B(T) + 2(1-x) \cdot (A(T) - B(T))), \quad A(T) = A_0 + A_1(\frac{T}{300 K} - 1), B(T) = B_0 + B_1(\frac{T}{300 K} - 1),
\]

while for NRTL, we follow the convention of Aspen DRS [8] according to 

\[
\frac{\mu}{RT}(x,T) = G_{f,01} + G_{f,02}(1-x) + x \ln(x) + (1-x) \ln(1-x) + x \cdot \frac{\tau_{12} \exp(-\alpha \tau_{12})}{x + \exp(-\alpha \tau_{12})} \cdot \frac{\tau_{12} \exp(-\alpha \tau_{12})}{(1-x) + x \exp(-\alpha \tau_{12})} \cdot \frac{\tau_{12}}{T} = A_{12} + F_{12}(\frac{T}{300 K} - 1), \quad \tau_{12}(T) = A_{21} + F_{21}(\frac{T}{300 K} - 1),
\]

where the reduced Gibbs free energies of formation \( G_{f,0i} \) at the pure, real liquid state with respect to the molar amount of species 1 are taken as constant over the pertinent temperature range. In order to achieve good scaling of the parameter values, we choose \( G_{f,01} = 1.0 \) and \( G_{f,02} = 1.5 \), as well as the reference temperature 300 K in the above given models. The case studies are based on some fictitious molecules 1 and 2. For the NRTL model, we set \( \alpha \) to a fixed value of 0.3, and for global optimization, variable bounds partially resulting from our choice of molar feed \( n_1^0 = 1 \text{ mol} \) and \( n_2^0 = 0 \text{ mol} \), according to \( A_0, A_{12} \in [-10.0, 10.0], A_1, F_{12} \in [-200.0, 200.0], B_0, A_{21} \in [-10.0, 10.0], B_1, F_{21} \in [-200.0, 200.0], x_i \in [\varepsilon_x, 1 - \varepsilon_x], n \in [1.0, 2.0], \) as well as \( b = 2 \text{ mol} \) for the elemental abundance vector (elemental feed), cf. Equation (2.1b). Having established the boundedness of the Lagrange multipliers \( \lambda \), cf. Appendix A.1, their bounds, as appropriate for global optimization, are determined. The fact that \( \lambda \) results from equality constraints (ECs) imposes a difficulty on determining the bounds. For \( MR = 1, N = 2 \), we estimate the range of the Gibbs free energy beforehand and then calculate the bounds \( \lambda \in [-1.0, 2.0] \) using Equation (4.2). In order to model an exothermic reaction, we regress to data chosen from Table 4.1, to regress to. Together with the above reported molar feed, the data delineate an increase in conversion with a decreasing temperature, covering a wide range of conversion. For another case study, we regress to data chosen from Table 4.2, cap-

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( x ) (mol mol(^{-1}))</th>
<th>( T ) (K)</th>
<th>( x ) (mol mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.05</td>
<td>301.0</td>
<td>0.6</td>
</tr>
<tr>
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<td>0.1</td>
<td>302.0</td>
<td>0.7</td>
</tr>
<tr>
<td>297.0</td>
<td>0.2</td>
<td>303.0</td>
<td>0.8</td>
</tr>
<tr>
<td>298.0</td>
<td>0.3</td>
<td>304.0</td>
<td>0.9</td>
</tr>
<tr>
<td>299.0</td>
<td>0.4</td>
<td>305.0</td>
<td>0.95</td>
</tr>
<tr>
<td>300.0</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4 Parameter Estimation in Reactive Systems

Table 4.2: Assumed measurements for the illustrative case study in Section 4.3.3 with respect to educt $Z_2$, in lieu of measurement data.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$x$ (mol mol$^{-1}$)</th>
<th>$T$ (K)</th>
<th>$x$ (mol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.925</td>
</tr>
<tr>
<td>299.0</td>
<td>0.875</td>
<td>302.0</td>
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</tr>
<tr>
<td>300.0</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

turing a smaller range of conversion. The RTPC is imposed on the LBP of the case studies in Sections 4.3.2 and 4.3.3, on the discrete sets $\hat{X}_{l,llp}^t = \{\epsilon_x, 0.1, 0.2, \ldots, 0.8, 0.9, 1-\epsilon_x\}$ and $\hat{X}_{l,llp}^t = \{\epsilon_x, 0.25, 0.5, 0.75, 1-\epsilon_x\}$, respectively. In order to avoid spurious phases, we choose $\hat{X}_{l,llp}^t = \{0.1, 0.2, \ldots, 0.8, 0.9\}$ and $\hat{X}_{l,llp}^t = \{0.25, 0.5, 0.75\}$, respectively. We initialize the discrete sets for the bilevel algorithm in such a way that convergence can be achieved after the first iteration. In addition, we set $\Delta_G = 1e-3$ and $\epsilon_x = 1e-4$ to close the strict IC (4.5) and open sets, respectively. We initialize the discrete sets for the bilevel algorithm in such a way that convergence can be achieved after the first iteration. In addition, we set $\Delta_G = 1e-3$ and $\epsilon_x = 1e-4$ to close the strict IC (4.5) and open sets, respectively, and $\Delta_x = 1e-5$. $LS = \sum_k \left( x_k^{\text{measured}} - x_k^{\text{predicted}} \right)^2$ is implemented as the objective function for data points $k = \{1, \ldots, 11\}$ and $k = \{1, \ldots, 5\}$, respectively. From the well-known linear transformation between the extent-of-reaction $\xi_{rc}$ of reaction $rc$ and the molar amount, $n_i = n_i^0 + \sum_{rc} \nu_{i,rc} \xi_{rc}$, $\forall i = 1, \ldots, N$, we derive the (nonlinear) relation between $x$ and $\xi$ for the figures in Section 4.3, according to $x = (n_i^0 + \nu_i \xi)/(n_i^0 + n_i^0 + \xi(\nu_i + \nu_2))$. The chemical reactor model is assumed to find, at least, local minima and reads $\min_{\xi} n(\xi) \cdot G(\xi)$ s.t. $\sum_i \nu_i \mu_{i,ph}(\xi) < 0.0004, \sum_i \nu_i \mu_{i,ph}(\xi) > -0.0004, \forall ph$. 4.3.2 Margules Model

In this section, we discuss parameter estimation of the reaction given by Equation (4.8) for the Margules model. In particular, we compare four different formulations of the parameter estimation problem, two of which are conventional NLPs, while the remaining ones are BLPs, cf. Section 4.2.1. In particular, in the following, we will advance from the NLPs to the BLPs by progressively adding constraints, in order to exclude erroneous results.

NLP Using KKT First-Order

The first formulation is given by the upper level of Problem (4.6) reduced to Equations (4.6a) to (4.6c); this is equivalent to regression subject to the well-known chemical reaction equilibrium constant, and we suspect that a similar formulation is used by [15, 21, 30] and [138]. For the parameter values obtained, Figure 4.1 illustrates the violation of the RTPC (Equation (2.5)) for the model prediction at 301 K. Furthermore, even the necessary second-order criterion for stability (Equation (2.9) based on [81]) is violated. In particular, since $\left( \frac{\partial^2 G}{\partial x^2} \right)_{x^*} = -3.33 < 0$, a maximum is erroneously obtained (cf. Appendix G.1). Indeed, plotting the results in the transformed variable space of the extent-of-reaction $\xi$ reveals the (local) maximum. In order to assess how those erroneous parameter values will affect results in the process simulation, we mimic the behavior of a typical chemical reactor model by solving the optimization problem given in Section 4.3.1. As shown in
4.3 Illustrative Case Studies

**Fig. 4.1:** RTPC (Equation (2.5)) is violated since this is not prevented by Equations (4.6a) to (4.6c), used for this figure. At 301 K for \( A = -4.707, B = 5.269 \) in the Margules model, a (local) maximum (\( * \)) is erroneously used during the regression. Left: reduced molar Gibbs free energy with respect to mole fraction of educt \( x_{Z_2} \), Gibbs free energy \( G(x_{Z_2})/(RT) \) (solid curve), reactive tangent plane \( \Theta(x_{Z_2}) \) (dashed line), predicted \( x_{Z_2} \) (\( * \)), target \( x_{Z_2} \) (\( \Delta \)), cf. Table 4.1, \( x_{Z_2} \) found by the chemical reactor model (\( \diamond \)). Right: reduced total Gibbs free energy with respect to extent-of-reaction \( \xi \), Gibbs free energy \( n(\xi) \cdot G(\xi)/(RT) \) (solid curve), predicted \( \xi \) (\( * \)), \( \xi \) found by the chemical reactor model (\( \diamond \)).

Figure 4.1, such a reactor model will, at least, find a local (\( x_{Z_2} = 0.376 \)), if not global (\( x_{Z_2} = 0.998 \)) minimum, which is significantly different from the model prediction used during the regression (\( x_{Z_2} = 0.576 \)). Therefore, the data in Table 4.1, i.e., the true extent-of-reaction at equilibrium, are demonstrably missed and the parameter values cannot be used. It should be emphasized that the global minimum at \( x_{Z_2} = 0.998 \) is the point of tangency of the supporting reactive tangent which satisfies the RTPC (Equation (2.5)). For more detailed regression and simulation results, see Appendix G.2.

**NLP Using KKT Second-Order**

As a next step, the erroneous behavior in the above presented section is suppressed by adding \( \left. \left( \frac{\partial^2 G}{\partial \xi^2} \right) \right|_{\xi^*} \geq 0 \) (Equation (2.9) based on [81]) as a constraint to the formulation, now comprising Equations (4.6a) to (4.6d). Solving the resulting NLP is probably close to [31] in terms of the method, since they use only local solvers. Figure 4.2 depicts the Gibbs curve for the obtained parameter values. Since we have \( \left. \left( \frac{\partial^2 G}{\partial \xi^2} \right) \right|_{\xi^*} \approx 0 \), a saddle is erroneously obtained (cf. Appendix G.1), which can be confirmed by plotting the results in the transformed variable space of \( \xi \). While the necessary criteria for stability are satisfied, the sufficient criterion in the form of the RTPC is not and thus, the predicted equilibrium state cannot be globally stable. Upon use of parameter values thus obtained in a chemical reactor model, the global minimum (\( x_{Z_2} = 0.998 \)) is found. As this is significantly different from the model prediction (\( x_{Z_2} = 0.457 \)) and the data in Table 4.1, the parameter values are again not applicable.
Fig. 4.2: RTPC (Equation (2.5)) is violated since this is not prevented by Equations (4.6a) to (4.6d), used for this figure. At 301 K for \( A = 0.1053, B = 5.261 \) in the Margules model, a saddle (\( \ast \)) is erroneously used during the regression. Left: reduced molar Gibbs free energy with respect to mole fraction of educt \( x_{Z_2} \), Gibbs free energy \( G(x_{Z_2})/(RT) \) (solid curve), reactive tangent plane \( \Theta(x_{Z_2}) \) (dashed line), predicted \( x_{Z_2} \) (\( \ast \)), target \( x_{Z_2} \) (\( \triangle \)), cf. Table 4.1, \( x_{Z_2} \) found by the chemical reactor model (\( \triangledown \)). Right: reduced total Gibbs free energy with respect to extent-of-reaction \( \xi \), Gibbs free energy \( n(\xi) \cdot G(\xi)/(RT) \) (solid curve), predicted \( \xi \) (\( \ast \)), \( \xi \) found by the chemical reactor model (\( \triangledown \)).

**BLP Using RTPC**

We now proceed to extend the above reported formulation to a BLP, given by Problem (4.6) with the RTPC as the only type of LLP. Solving the resulting BLP seems to represent in some regards the method in [168], provided that their algorithm converges. Inspection of the Gibbs curve obtained from the regressed parameter values reveals that the RTPC is satisfied, cf. Figure 4.3; however, a spurious phase is predicted since there is more than one point of tangency, yet the reaction system is known to be single-phase. In the transformed variable space of \( \xi \), this erroneous behavior is equivalent to the existence of a second global minimum [29] left to the one used during regression. (Both minima are global in the sense that their objective values are equal within a tolerance of 3e-4, cf. Appendix G.2.) Since a second liquid phase implies both phase and chemical reaction equilibrium, it contradicts the data in Table 4.1. Furthermore, using these erroneous parameter values, a chemical reactor can yield the undesired minimum \( (x_{Z_2} = 0.915) \) instead of the desired one which is used during the regression \( (x_{Z_2} = 0.577) \), or can even report a two-phase regime. Again, the data in Table 4.1 would not be represented in such a process simulation.

**Full BLP Formulation**

As a consequence of the issues presented in the previous section, we further tighten the problem and add Equation (4.5) as another type of LLP to Problem (4.6), finally yielding the full problem formulation proposed in this thesis. Solving the respective BLP yields parameter values which result in the Gibbs curve presented in Figure 4.4. From the figure it is apparent that satisfaction of both sufficient and necessary criteria for stability, in ad-
4.3 Illustrative Case Studies

Fig. 4.3: Equation (4.5) is violated since this is not prevented by Problem (4.6) including the RTPC (2.5) as the only type of LLP, which is used for this figure. At 301 K for $A = -1.004, B = 2.277$ in the Margules model, the global minimum of Gibbs free energy ($\ast, \triangle$) is erroneously not unique. Left: reduced molar Gibbs free energy with respect to mole fraction of educt $x_{Z_2}$, Gibbs free energy $G(x_{Z_2})/(RT)$ (solid curve), reactive tangent plane $\Theta(x_{Z_2})$ (dashed line), predicted $x_{Z_2}$ ($\ast$), target $x_{Z_2}$ ($\triangle$), cf. Table 4.1, $x_{Z_2}$ found by the chemical reactor model ($\approx$). Right: reduced total Gibbs free energy with respect to extent-of-reaction $\xi$, Gibbs energy $n(\xi) \cdot G(\xi)/(RT)$ (solid curve), predicted $\xi$ ($\ast$), $\xi$ found by the chemical reactor model ($\approx$).

Fig. 4.4: The unique global minimum ($\ast$) is correctly used during the regression, due to Problem (4.6) with all LLPs included, as shown for $A = -0.9871, B = 1.743$ in the Margules model at 301 K. Left: reduced molar Gibbs free energy with respect to mole fraction of educt $x_{Z_2}$, Gibbs free energy $G(x_{Z_2})/(RT)$ (solid curve), reactive tangent plane $\Theta(x_{Z_2})$ (dashed line), predicted $x_{Z_2}$ ($\ast$), target $x_{Z_2}$ ($\triangle$), cf. Table 4.1, $x_{Z_2}$ found by the chemical reactor model ($\approx$). Right: reduced total Gibbs free energy with respect to extent-of-reaction $\xi$, Gibbs free energy $n(\xi) \cdot G(\xi)/(RT)$ (solid curve), predicted $\xi$ ($\ast$), $\xi$ found by the chemical reactor model ($\approx$).
Fig. 4.5: RTPC (Equation (2.5)) is violated since this is not prevented by Equations (4.6a) to (4.6c), used for this figure. At 302 K for $\tau_{21} = 5.672, \tau_{21} = -1.162$ in the NRTL model, a (local) maximum (*) (close to a local minimum (♦)) is erroneously used during the regression. Left: reduced molar Gibbs free energy with respect to mole fraction of educt $x_{Z_2}$, Gibbs free energy $G(x_{Z_2})/(RT)$ (solid curve), reactive tangent plane $\Theta(x_{Z_2})$ (dashed line), predicted $x_{Z_2}$ (*), target $x_{Z_2}$ (△), cf. Table 4.1, $x_{Z_2}$ found by the chemical reactor model (♦). Right: reduced total Gibbs free energy with respect to extent-of-reaction $\xi$, Gibbs free energy $n(\xi) \cdot G(\xi)/(RT)$ (solid curve), predicted $\xi$ (*), $\xi$ found by the chemical reactor model (♦).

In addition to the correct number of phases, can be achieved. In other words, in the transformed variable space of $\xi$, only the BLP formulation is capable of enforcing a unique global minimum at the model prediction. As desired, the chemical reactor model will correctly find this very model prediction ($x_{Z_2} = 0.598$), i.e., the true extent-of-reaction at equilibrium, in agreement with the data in Table 4.1. In contrast, Figures 4.1 and 4.2 demonstrate some serious issues with conventional formulations. While these formulations give lower least-square errors, cf. Appendix G.2, they fail to satisfy thermodynamic stability.

4.3.3 NRTL Model

In this section, we discuss parameter estimation of the reaction given by Equation (4.8) for the NRTL model. Using the conventional problem formulation comprising Equations (4.6a) to (4.6c), parameter values are obtained which imply the undesired behavior shown in Figure 4.5. That is, a (local) maximum is erroneously used during the regression, violating even the second-order necessary criterion for stability, cf. Equation (2.9) in [81]. As discussed earlier, in the process simulation, either local ($x_{Z_2} = 0.987$) or global ($x_{Z_2} = 0.595$) minima are found. While the first is close to the model prediction used during the regression ($x_{Z_2} = 0.950$) and thus, less problematic, a reliably working unit operation model will miss it and correctly return the global one instead. However, this simulation result will not correspond to the data in Table 4.2.

We directly proceed to the full BLP formulation given by Problem (4.6), with which the desired behavior is eventually obtained as depicted in Figure 4.6. As desired, the data are represented by the regression results, which coincide with the process simulation results at
4.3 Illustrative Case Studies

Fig. 4.6: The unique global minimum (⋆) is correctly used during the regression, attributed to Problem (4.6) as shown for τ_{12} = 2.877, τ_{21} = −0.3439 in the NRTL model at 302 K. Left: reduced molar Gibbs free energy with respect to mole fraction of educt \( x_{Z_2} \), Gibbs free energy \( G(x_{Z_2})/(RT) \) (solid curve), reactive tangent plane \( \Theta(x_{Z_2}) \) (dashed line), predicted \( x_{Z_2} \) (⋆), target \( x_{Z_2} \) (△), cf. Table 4.1, \( x_{Z_2} \) found by the chemical reactor model (⋆). Right: reduced total Gibbs free energy with respect to extent-of-reaction ξ, Gibbs free energy \( n(ξ) \cdot G(ξ)/(RT) \) (solid curve), predicted ξ (⋆), ξ found by the chemical reactor model (⋆).

the global minimum of the LLP (\( x_{Z_2} = 0.946 \)). For more detailed regression and simulation results, see Appendix G.2.

4.3.4 Discussion

Figures 4.1 to Figure 4.3 and 4.5, along with Table 4.3, demonstrate the need for the BLP formulation (Problem (4.6)): it mathematically guarantees that the predicted mole fraction is the unique global minimizer of the Gibbs free energy. The BLP does not necessarily enforce that there exist no stationary points other than the unique global minimum as might be inferred from Figures 4.4 and 4.6. Similarly, the impression that the satisfaction of thermodynamic constraints will come at the cost of goodness of fit is an issue for these particular case studies, cf. Appendix G.2. In general terms, however, parameter bounds can be chosen more appropriately, allowing good fits with the BLP.

In contrast to the BLP, conventional regression formulations do not prevent spurious phases and/or missing the global minimum of the Gibbs free energy during the regression. In particular, we show that parameter estimation subject to the chemical reaction equilibrium constant (Equation (2.8) employed as Equation (4.6b)) entails erroneously using a local maximum of the Gibbs free energy. Assuming a chemical reactor model that relies on, at least, local minimization, we demonstrate that these incorrect parameter values propagate to incorrect values of the extent-of-reaction at equilibrium in the simulation, cf. Sections 4.3.2 and 4.3.3.

Advancing from our illustrative example to real-world case studies, the implications are as follows: If those parameter values that imply a violation of the RTPC (cf. Figures 4.1, 4.2, 4.5) were used by other research groups, e.g., in state-of-the-art process simulators
Table 4.3: Case study results of Sections 4.3.2 and 4.3.3. Only with the full BLP formulation (Problem (4.6) incl. (2.5) and (4.5)), the regressed parameter values are applicable in a chemical reactor model. In contrast, a formulation based on the chemical reaction equilibrium constant or variations of it (Equations (4.6a) to (4.6c)) gives incorrect parameter values.

<table>
<thead>
<tr>
<th>Case study</th>
<th>Regression formulation</th>
<th>Stationary point</th>
<th>Applicable in reactor model?</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
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<td></td>
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<td>yes</td>
</tr>
</tbody>
</table>

Incorporating chemical reactor models [58, 174], or reactive distillation [68], they would lead to erroneous values of the extent-of-reaction at equilibrium, even when the Gibbs free energy has been globally minimized by the groups. (Issues with chemical reactor models which rely on solving Equation (2.8) rather than minimization are equally severe. Undesired solutions due to a sub-optimal Gibbs free energy are discussed by [22, 29, 56, 74, 95, 123].) Perhaps more importantly, incorrect parameter values can demonstrably lead to spurious phases, cf. Figure 4.3, and the process simulator might proceed to rely on a two-phase flow, when, in fact, it is single-phase. In the worst case, this will entail erroneous modeling decisions in conceptual process design, e.g., spurious decanters and extraction columns. Similarly, a process simulator might identify extents-of-reaction at equilibrium which are well below the true values, cf. Figures 4.1 and 4.2. Based on these seemingly low extents-of-reaction, the modeler might erroneously decide to employ recycle streams. Both spurious recycles and apparatus will result in gratuitously higher investment costs. While in the present work, these issues are demonstrated for simple case studies, the root of the problem is methodological in nature and, as such, not restricted to particular (nonconvex) Gibbs models, measurement data, fluid systems, phase types, nor chemical reactions. Furthermore, the demonstrated error will, in our opinion, probably become an issue at least as severe for problems of higher dimensionality, i.e., multi-component and multi-reaction systems.

4.4 Interim Conclusions

In this chapter, we demonstrate that regression subject to the well-known chemical reaction equilibrium constant can entail the violation of thermodynamic stability. As a consequence, erroneous values of the extent-of-reaction at equilibrium are obtained upon use of the respective parameter values in chemical reactor models in, e.g., process simulation. As opposed to conventional programs, a BLP allows parameter regression for reactive systems, subject to the necessary and sufficient criteria for the satisfaction of thermodynamic stability, based on Smith and Jiang’s RTPC [81, 80, 154].

As a special feature of the formulation proposed in this chapter, there is a mathemati-
4.4 Interim Conclusions

cal guarantee of satisfying stability, along with the correct number of phases as observed from experiments, for the parameter values resulting from the regression. In contrast, conventional methods are numerically less involved, yet risk a violation of these criteria. Several such formulations are compared by an illustrative single-phase dimerization reaction, demonstrating the advantages of the BLP in terms of thermodynamic stability, while the conventional formulations provide better least-square errors, yet fail to meet stability. Therefore, in our opinion, the goodness of fit should, thus, not be considered the only indicator of a successful regression, nor should a certain Gibbs model be discarded due to undesired behavior. On the contrary, it is important that the constraints of the regression problem are satisfied (bilevel-feasibility), in the form of those criteria that are necessary and sufficient for stability. In the mathematical context of Chapter 2, only the full BLP yields a solution \((\mathbf{x}^{u,*}, \mathbf{q}^{u,*})\) of Problem (4.6) which provides the desirable guarantee that a reliable chemical reactor model correctly regain \(\mathbf{x}^{u,*}\) upon use of \(\mathbf{q}^{u,*}\) for a nonideal reaction system.

To date, for higher-dimensional problems, that is, those with multiple reaction invariants (chemical elements) and ternary or even multi-component (electrolyte) mixtures, the subproblems of the bilevel algorithm do not seem computationally tractable when employing state-of-the-art commercial solvers, such as BARON [161]. Further work will be concerned with the special case of reactions at constant total molar amount, as this involves a modified RTPC [80], as well as industrial fluid systems, in order to compare to the literature. Finally, these problems shall be implemented in the regression tool BOARPET [109] in the future.
5 Parameter Estimation of Cubic Equations of State (CEOS)

Disclaimer: This chapter (except for Section 5.2) adopts the abstract and the following sections from [60]: parts of “Introduction”, parts of “Spurious phases reported in the literature”, parts of “Conclusion and outlook”, as well as the full sections “Problem formulations”, “Proposed bilevel program”, “Materials and methods”, and “Results”. Contributions to [60]: Hatim Djelassi proposed to formulate the LLPs as MINLPs and to introduce a dependent variable. He helped to improve the author’s problem formulations, contributed the main part of the section “Algorithm”, and gave some advice on notational and convergence issues, in order to comply with [43]. The author wrote the manuscript, proposed the method, formulated the (sub-)problems, implemented the algorithm in [43] and the required extensions in BOARPET stand-alone, and performed the case studies and the calculations in Aspen Plus. It should be noted that this thesis includes corrections of [60], in particular the inconsistent mixing rule from literature is removed from Appendix J.2.1. Acknowledgment: The author would like to thank Ulrich K. Deiters for some helpful advice on the solution of cubic equations in thermodynamic models, and Nick Sahinidis for his in-depth feedback on the performance of BARON for her lower-level problem files. It should be noted that an early version of this section is used by Johannes-Robert Bruch [26] in the form of a technical report, namely “Bilevel Programming in Parameter Estimation of Cubic Equations of State”.

As mentioned at the beginning of Chapter 4, both in academia and industry, parameter estimation methods consider, at best, a posteriori checks for thermodynamic stability and its variations, and commonly, do not present a systematic correction in the case of its violation. This also applies to regressing cubic equations of state (CEOS) models. Besides the regression tools mentioned in Chapter 4, we would also like to point out ThermoC [39] which is dedicated to regressing versatile equations of state. To the author’s best knowledge, within those tools, the roots to the CEOS are commonly not discriminated such that thermodynamic stability is guaranteed. Similar regression techniques can be found in the literature, e.g., [149] estimate binary interaction parameters of Peng-Robinson (PR), Soave-Redlich-Kwong (SRK) and a General Equation of State for a binary VLLE, subject to isopotential. Furthermore, some regression methods are not even guaranteed to satisfy necessary criteria for stability. For instance, [89] minimize the violation of isopotential when fitting NRTL combined with PR. Altogether, it seems common practice to fit CEOS models to phase equilibrium data without considering thermodynamic stability rigorously during the regression.

This can lead to quantitatively and/or qualitatively incorrect results, for any model of the Gibbs and Helmholtz free energy if nonconvex in mole fraction. In particular, some prevalent CEOS models exhibit evidentially nonconvex terms [49, 72, 87] which can make the effect of such erroneous results quite pronounced. For instance, [9] observe a spurious miscibility gap when regressing binary VLE data of refrigerant mixtures for the SRK model, subject to isopotential. In order to suppress this false behavior, they do not regress the binary interaction parameter for the covolume, cf. Section 5.1.1. [164] report three phases in equilibrium when regressing VLE data of water/organic species systems with
PR, SRK and Trebble-Bishnoi CEOS (TB [163]), subject to (most probably local) flash or dew and bubble point calculations. They suggest to more strictly constrain the parameter ranges and/or to regress larger amounts of data including LLE data, cf. Sections 5.1.2 and 5.1.3. Similarly, [148] perform a regression using SRK with Mathias modification [96] and Huron-Vidal mixing rules in Aspen Plus, and report a spurious LLE. [148] attribute this undesired behavior to the applied mixing rule. Considering the relation of the mixing rule to $\Delta G^E$-models a spurious LLE might not seem surprising although Huron and Vidal report suppression of this very behavior in some cases [79]. Obviously, other regression methods need to be taken into account and as a side, yet important note, [148] remark the potential inadequacy of the regression method in Aspen Plus, followed by a proposal for a particular constraint to avoid spurious LLEs. In essence, this yields a BLP for parameter estimation (though simply denoted as “constrained regression technique” in [148]). Pursuing the idea of “constrained minimization” [47, 48] seem to reformulate the constraint in [148], cf. Section 5.3.2. While these latter works already introduce certain ideas of parameter estimation in bilevel programming which are successfully implemented by others [122, 121, 171], they do not address all potential issues as will be discussed in Section 5.3.2. Altogether, in the literature, various causes are associated with the prediction of incorrect phase behavior of CEOS, such as the number of parameters [9, 164], the type and amount of measurement data [164, 171], the fluid system [148] and the CEOS model-mixing rule combination [48, 79, 121, 148, 175]. However, in our opinion, it is primarily the adequacy of the regression technique that is, the regression problem formulation plus the optimization algorithm(s) applied which should be questioned when observing incorrect thermodynamic behavior for the fit obtained. The reason for this is that a rigorous technique, i.e., a regression subject to necessary and sufficient criteria for thermodynamic stability and other desired behavior does not exhibit the aforementioned pitfalls, as demonstrated by our earlier works for excess Gibbs free energy ($\Delta G^E$) models [107, 108, 20, 59].

This motivates the need for the extension of the methods in [107, 108, 20, 59] to the regression of CEOS models; we are considering both symmetric and asymmetric models. What makes the technique involved is the fact that thermodynamic stability constrains the regression problem, making it into a BLP with several LLPs. In the context of CEOS models, the BLP embeds thermodynamic stability with respect to both the phase and mechanical equilibrium; this is done in the present chapter.

It is well-known that real-gas properties captured by the CEOS, such as the molar covolume cannot be modeled using the ideal gas. As a consequence, the VLE formulations in [20] are not special cases of the formulations proposed in this thesis. Our formulations may also be seen as an augmentation of the methods in [148] and [47], namely to determine CEOS parameters subject to special constraints. In this work, these represent constraints in the form of LLPs. For the formulations, we choose the criterion in [12] and results from [72], as embedding it in a BLP structure is straightforward, yet most likely at the cost of CPU time. Finally, cubic equality is imposed on the lower level calling for algorithmic changes to [107, 108, 20]. This is taken into account in [43].

The outline of this chapter is as follows: This introduction is followed by Section 5.1 in which certain results from the literature are recreated and used in the process simulation, in order to illustrate the fatal consequences of standard parameter estimation. We insert Section 5.2 to introduce a criterion for root discrimination which is used in the problem formulations given in Section 5.3.1. After a review of particular approaches from the
literature to overcome these deficiencies in Section 5.3.2, a BLP formulation is proposed in Section 5.4, and contrasted to the formulations given in the prior sections. In Section 5.5, we demonstrate the advantages over standard methods by the VLE of C$_5$H$_{12}$/H$_2$S for both PR and SRK, followed by interim conclusions in Section 5.6. Further, see Appendix J for a formal proof that Baker’s criterion is applicable to the extended variable space of CEOS models without any modifications, in order to ensure the fulfilment of phase stability. Appendix J closes with a trilevel formulation of the parameter estimation problem and details on the CEOS models and the regression results.

5.1 Motivation: Spurious Phases

In the previous section, we outline some specific, undesired behavior which the literature reports to result from regression. Spurious liquid phases seem to be most prevalent (cf. Figures 2.1b,c); this is expected since CEOS are models with the desired ability to capture also LLE phenomena [73]. See Figure 2.1 where all of such undesired configurations are assembled. In this section, we seek to graphically and numerically prove or disprove specific claims in the open literature. We do this by recreating the reported results, at least, qualitatively, in terms of Gibbs free energy curves, and by interpreting those with the criterion in [12]. The numerical results of flash simulations using RGibbs through Aspen Plus [7], also see Section 5.5.1 serve the purpose of highlighting the consequences of erroneous regression results for the process simulation. The focus is on a variety of erroneous phenomena, that is, both distinct spurious phases and spurious phase splits.

5.1.1 CF$_4$/CHF$_3$

[9] mention a spurious LLE for their regression of the VLE of CF$_4$/CHF$_3$ to SRK for certain parameter values, and report to have resolved the issue for a different choice of parameter configuration. For the latter, we closely inspect Figure 5.1 to find that the Gibbs free energy of the liquid phase is erroneously linear, if not slightly nonconvex. Indeed, giving this as a flash problem to RGibbs for the feed $x_{\text{CF}_4} = 0.5$, RGibbs reports an LLE, where $x_{\text{CF}_4,I} = 0.38499$ and $x_{\text{CF}_4,II} = 0.5938$. This contradicts the experimental data; in particular, the LLE is known to close at the upper critical solution temperature (UCST) at 131.4 K [33]. The reason for this is that the erroneous nonconvexity of $G_{\text{liquid}}(x_{\text{ph},i})$ on $(x_{\text{CF}_4,I}, x_{\text{CF}_4,II})$ is, at least, for the implementation in Aspen Plus [7] and its potential round-off errors, actually not prevented by the regression formulation from the literature. Altogether, in our opinion, the parameter values recommended in [9] should not be applied above the critical point since they can lead to erroneous process simulation results.

5.1.2 Acetone/Water

We can confirm the spurious LLE that [164] report for their regression of the narrow-boiling VLE of acetone/water for PR. A close inspection of Figure 5.2 reveals that the Gibbs free energy of the liquid phase is erroneously nonconvex. Again, giving this as a flash problem to RGibbs for the feed $x_{\text{C}_3\text{H}_6\text{O}} = 0.4$, RGibbs reports an LLE, where $x_{\text{C}_3\text{H}_6\text{O},I} = 0.27448$ and $x_{\text{C}_3\text{H}_6\text{O},II} = 0.44173$, although only the VLE is observed in the experiments [67]. Similar observations can be made for SRK for a slightly different parameter value ($k_{a,ij} = -0.202$)
5.1 Motivation: Spurious Phases

Fig. 5.1: Gibbs free energy $\Delta G$ with respect to mole fraction of CF$_4$ at 145.16 K, 100.616 kN m$^{-2}$, for VLE of CF$_4$/CHF$_3$ with $k = 0.0954, k' = 0$ for SRK from [9].

Fig. 5.2: Gibbs free energy $\Delta G$ with respect to mole fraction of acetone at 373.124 K, 266.827 kN m$^{-2}$, for VLE of acetone/water with $k_{a,ij} = -0.2033$ for PR from [164].
Fig. 5.3: Gibbs free energy $\Delta G$ with respect to mole fraction of methanol at 301.7 K, 30.731 kN m$^{-2}$, for VLE of methanol/benzene with $k_{a,ij} = 0.0927$ for PR from [164].

which is in agreement with [79]. The reason for this is that the erroneous nonconvexity of $G_{\text{liquid}}(x_{\text{ph}}, \cdot)$ on $(x_{\text{C}_3\text{H}_6\text{O}, \text{I}}, x_{\text{C}_3\text{H}_6\text{O}, \text{II}})$ is not prevented by the regression formulation from the literature.

5.1.3 Methanol/Benzene

[164] report a spurious second liquid phase for their regression to capture the homogeneous azeotrope of methanol/benzene with PR and SRK. Indeed, Figure 5.3 reveals that the Gibbs free energy of the liquid phase is erroneously nonconvex, and for the feed $x_{\text{CH}_3\text{OH}} = 0.5$, RGibbs reports an LLE, where $x_{\text{CH}_3\text{OH}, \text{I}} = 0.34560$ and $x_{\text{CH}_3\text{OH}, \text{II}} = 0.93137$, although there is experimental evidence only for a VLE [160]. Furthermore, for the very same settings, yet a different feed $x_{\text{CH}_3\text{OH}} = 0.6$, RGibbs reports a VLE, where $x_{\text{CH}_3\text{OH}, \text{III}} = 0.35608 \approx x_{\text{CH}_3\text{OH}, \text{I}}$ and $x_{\text{CH}_3\text{OH}, \text{IV}} = 0.62263$. This highlights the risk of a process simulator to erroneously interpret the phase behavior as a(n) LLE/VLLE which is both quantitatively and qualitatively incorrect and due to a standard regression method. Similar observations can be made for SRK with $k_{a,ij} = 0.1034$ which is in agreement with [164]. We would like to add that in terms of RGibbs, this small numerical study reveals that it implements only local solvers and its results can, even qualitatively, strongly depend on initialization.

5.2 Thermodynamic Stability and Root Discrimination

Disclaimer: This section is an abridged version of [62], in particular, it adopts the abstract and the sections entitled “Introduction”, “Proposed root discrimination formulation based on Cardan’s method”, “Root discrimination formulation based on thermodynamics”, “Analysis and application to case studies”, and “Conclusions and outlook”. It should be noted that the author added the distinction between sub- and super-critical states to the discussion of [46, Figure 2]; this was wrong in [62]. Acknowledgment: The
In order to develop a methodology for parameter estimation of CEOS models, special care needs to be taken when incorporating the mechanical equilibrium. In a purely mathematical context, this translates to the question of how to select the correct root in the presence of multiple real roots to a cubic equation. This discussion is not restricted to parameter estimation only, and several discrimination criteria have been proposed. This section introduces a criterion which exploits the well-known method of Cardano to solve cubic equations. The criterion is straightforward, continuous and covers different root scenarios. As a reference, the minimization of the Gibbs free energy (mechanical equilibrium) is formulated for $P, T = \text{const}$. From its KKT conditions, it follows an implication for mixtures that change from a two-phase to a single-phase state. In such a case, the CEOS is not imposed as an equality constraint any more, i.e., cubic equality is relaxed as an alternative to relaxation of root discrimination as proposed in [83]. The proposed criterion and those from the literature, at best, satisfy a necessary condition, while the minimization of the Gibbs free energy obviously is a necessary and sufficient condition for thermodynamic stability of the selected root. In certain cases, formulations from the literature are found to exclude valid solutions, whereas the proposed criterion overcomes this deficiency.

### 5.2.1 Need for Root Discrimination

CEOS exhibit one to three real roots of molar volume or related variables. If there are multiple real roots, one needs to select the correct one, in order to calculate thermodynamic properties, such as fugacities, and state variables, such as the Gibbs free energy for, e.g., phase envelope calculations. Hence, a root discrimination criterion is required. [32] propose a root discrimination criterion for the Soave-Redlich-Kwong (SRK) CEOS that is based on mathematical properties of cubic equations, in particular stationary values. [69] extends the criterion to Peng-Robinson (PR) CEOS without generalizing to all types of CEOS, nor discussing the direct relation to the well-known method of Cardano, see e.g., [119, 40]. [40] and the follow-up [41] use Cardano’s method to propose algorithms for solving CEOS for the density roots. However, these algorithms cannot directly be reformulated to a concise, single root discrimination criterion. [136] develop a criterion based on isothermal compressibility (not to be confused with the compressibility factor $Z_r$), in order to classify a root as liquid- or vapor-like. Some failures of the criterion are discussed and no mathematical proof is presented. [125] extend this criterion to the single-real-root region and the respective follow-up [169] is implemented in Aspen DRS [8]. [176] argue that the liquid-like root may be excluded by restricting the compressibility factor $Z_r$ to $[0.5, 1.0]$. [83] propose and prove a continuous root discrimination criterion based on first- and second-order derivatives of the cubic function with respect to the compressibility factor; they detach the problem from its thermodynamic motivation and to focus on its mathematical features only. The criterion is also embedded in the phase equilibrium formulation in [65] such that root discrimination is relaxed if a phase vanishes (not necessarily at a critical point). [46] overhaul the criterion in [83] by applying thermodynamic criteria, such as the critical point, along with dew and bubble point curves. These thermodynamic criteria are used to further relax the root discrimination criterion in [83]. Altogether, to
the author’s best knowledge, in the literature, there exists no method that can both be formulated as a root discrimination criterion and would fully exploit the calculus of cubic equations, in order to determine the number of real roots. In addition, there is no special focus on sufficient criteria for thermodynamic stability.

In this section, an alternative root discrimination criterion is proposed, with a more direct relation to the number of real roots to a CEOS. The criterion is based on Cardano’s method and the criterion in [83]. In particular, the new criterion exploits the relation between the discriminant and the derivatives of a cubic equation, resulting in a continuous formulation based on simple calculus. The criterion is straightforward and, unlike other methods, does not exclude valid points, if embedded in an optimization problem or a simulation.

In addition, root discrimination based on thermodynamic stability is analyzed. Specifically, global optimization of the Gibbs free energy is discussed and it is demonstrated by means of the KKT first-order conditions that this root discrimination formulation allows for three important results. First, this opens an alternative derivation of a tangent plane criterion for the Helmholtz free energy. Second, a formulation which is applicable to the case of mixtures that change from a two-phase to a single-phase state is proposed, as an alternative to the formulation in [83]. Finally, a well-known root discrimination criterion that satisfies the necessary conditions for thermodynamic stability, i.e., a negative slope of the isotherm in the \((P, v)\)-diagram, may be deduced. However, this latter criterion does not guarantee thermodynamic stability.

In Section 5.2.2, a root discrimination criterion based on Cardano’s method is proposed. In Section 5.2.3, an alternative root discrimination is formulated as a \((P, T)\)-flash problem and implications of its KKT first-order conditions are discussed. Further root discrimination criteria from the literature are analyzed in Section 5.2.4 by comparing these to the criteria presented in Sections 5.2.2 and 5.2.3. After a conclusion in Section 5.2.5, we include the aforementioned KKT first-order conditions in Appendix H.1, an analysis of further criteria from the literature in Appendix H.2, a short proof of a particular conjecture in [136] and [46] in Appendix H.3, and finally, a discussion on constraint qualifications (CQs) of the criterion proposed in this section and the criterion in [83] considered as stand-alone, to be found in Appendix I.

### 5.2.2 Proposed Root Discrimination Formulation

In this section, a root discrimination criterion based on Cardano’s method, see e.g., [119], is proposed; it exhibits some useful properties required for, e.g., parameter estimation of CEOS, subject to specific constraints. In particular, one of these properties is how the criterion handles the case in which the desired root does not exist.

[69] proposes to replace the nonexistent root by the stationary values of the cubic equation that are closest which is also what [24] seem to suggest after limited success with particular constraints on the volume roots. However, cubic functions are not guaranteed to exhibit stationary values. Similarly, [136] perturb temperature and pressure in a particular fashion until the desired root appears. Finally, [177] propose the extrapolation of thermodynamic state variables and properties from the three- to the single-real-root region, yet the physical significance of the extrapolated properties is not checked for. The consequences of a nonexistent root for a vanishing phase are discussed in [83]; however, the more relevant case of a nonexistent root for the existent phase does not seem to be considered. This will be covered in Section 5.2.4.
In contrast, the formulation presented in this section will always yield a root, however, at the expense of satisfaction of CQs, see Appendix I. In particular, in the single-real-root region, the criterion will yield the only existent root, even if it is not of the desired type. It should be noted that, although this strategy is reported to complicate convergence when embedded in specialized flash algorithms [24], it is in agreement with the minimization of the Gibbs free energy, see Section 5.2.3. Most importantly, this implies that the criterion does not exclude valid points. Furthermore, the proposed criterion is continuous and based on the calculus of cubic equations. Finally, we will briefly discuss the consequences of violating CQs. In Appendix I, it is demonstrated that an optimization problem subject to the proposed formulation violates certain CQs in, e.g., the single-real-root case. This implies that the KKT first-order conditions are no longer necessary for a globally optimal point. Hence, when applying an optimization algorithm to such a problem, the algorithm may erroneously exclude the globally optimal solution point and thus, there is a risk to erroneously interpret locally optimal points as globally optimal. This error is of type false positive, as unstable states may be spuriously assumed to be stable. From a technical perspective, in a branch-and-bound algorithm the upper bound (UBD) may fail due to violation of CQs. However, upon convergence, the true global optimum will be found within a predefined optimality gap $optca / optcr$, provided the lower bound (LBD) is valid. Consequently, said violation of CQs is assumed not to affect the results.

**Statement of Proposed Root Discrimination**

Let $f_{ceos}(x_{ph}, v_{ph,r}) : \mathbb{R}^{n_i} \rightarrow \mathbb{R}$ denote a continuously differentiable function that is cubic with respect to $v_{ph,r}$ and stated in the form proposed in [83], and $\left( \frac{\partial^2 f_{ceos}}{\partial v^2} \right)_{x_{ph},\cdot} : \mathbb{R}^{n_i} \rightarrow \mathbb{R}$ the $i$th-order derivative of $f_{ceos}$ with respect to $(\cdot)$, evaluated at $(x_{ph},\cdot)$. It should be noted that the feasible set of roots $v_{ph,r}$ is to be restricted to physical solutions, i.e., greater than the covolume as pointed out by, e.g., [85]. In the following, the parameters of the cubic function are considered constant. The proposed root discrimination is based on the formulation in [83] and Cardano’s method, see e.g., [119]. For a phase of composition $x_{ph}$, the criterion is given by

\begin{align*}
    f_{ceos}(x_{ph}, v_{ph,1}) &= 0 \quad (5.1a) \\
    f_{ceos}(x_{ph}, v_{ph,3}) &= 0 \quad (5.1b) \\
    - \left( \frac{\partial f_{ceos}}{\partial v} \right)_{x_{ph},v_{ph,1}} &\leq 0 \quad (5.1c) \\
    - \left( \frac{\partial f_{ceos}}{\partial v} \right)_{x_{ph},v_{ph,3}} &\leq 0 \quad (5.1d) \\
    -D(x_{ph}) \cdot \left( \frac{\partial^2 f_{ceos}}{\partial v^2} \right)_{x_{ph},v_{ph,1}} \cdot \left( \frac{\partial^2 f_{ceos}}{\partial v^2} \right)_{x_{ph},v_{ph,3}} &\leq 0 \quad (5.1e) \\
    v_{ph,3} - v_{ph,1} &\leq 0. \quad (5.1f)
\end{align*}

Altogether, this results in a set of 6 nonlinear equations in the 3 continuous variables $x_{ph}$, $v_{ph,1}$, $v_{ph,3}$. As a drawback of Equation (5.1e), Criterion (5.1) will exhibit a bad scaling as soon as any of the terms on the LHS gets close to zero. Using the sign-function would alleviate the problem, yet introduce a discontinuity. Alternatively, Equations (5.1e) and
5 Parameter Estimation of Cubic Equations of State (CEOS)

Fig. 5.4: Root scenarios in a \((P,T)\)-diagram of a mixture of fixed feed composition, also see, e.g., [141, Figure 8-17]. Dotted region indicates case of three distinct real roots, discriminant \(D(x_{ph}) < 0\). Plain region illustrates case of a single real root, \(D(x_{ph}) > 0\). Three coinciding roots at point 2 (so-called pseudo-critical point). Two coinciding roots on lines 1-2 and 2-3, excluding point 2. The latter cases imply \(D(x_{ph}) = 0\). Dew and bubble curves, and critical point are not shown.

\[(5.1f)\) may be reformulated using a binary variable \(\theta_i \in \{0, 1\}\), and constants \(M_i \in \mathbb{R}_{>0}\) which are sufficiently large to relax the following constraints, according to

\[
\begin{align*}
D(x_{ph}) - \theta_i \cdot M_1 & \leq 0 \\
-D(x_{ph}) - (1 - \theta_i) \cdot M_2 & \leq 0 \\
-\left(\frac{\partial^2 f_{ceos}}{\partial v^2}\right)_{x_{ph},v_{ph,1}} & - \theta_i \cdot M_3 \leq 0 \\
-\left(\frac{\partial^2 f_{ceos}}{\partial v^2}\right)_{x_{ph},v_{ph,3}} & - \theta_i \cdot M_4 \leq 0.
\end{align*}
\]

This results in a set of 8 nonlinear equations in 4 variables one of which is binary. In particular, \(\theta_i = 0\) represents the case of \(D(x_{ph}) \leq 0\), that is, there exist up to three real distinct roots according to Cardano’s method. Equations (5.2c) and (5.2d) will then discriminate between the roots. On the other hand, \(\theta_i = 1\) represents the case of \(D(x_{ph}) \geq 0\), that is, there exist one to two distinct real roots according to Cardano’s method, and root discrimination is not imposed. In Appendix I, it is shown that Criterion (5.2) is less likely to violate CQs than Criterion (5.1). In the following, only Criterion (5.1) will be discussed, as it offers the advantageous property of continuity.

**Proposition 1** Assume the root scenarios of a single real root, three distinct real roots, and three coinciding real roots. For given \((P,T,x_{ph})\), Criterion (5.1) will yield all those roots \(v_{ph,r}\) that satisfy the necessary condition for thermodynamic stability.

In the remaining case of two distinct real roots, however, the criterion is not guaranteed to give the complete set of those roots as discussed below. For a proof, the reader is referred to [83] and Cardano’s method. The criterion works as follows, also see Figure 5.4 for illustration:
5.2 Thermodynamic Stability and Root Discrimination

**Single Real Root.** In the single-real-root region, \( D(x_{ph}) > 0 \) according to Cardano’s method. Then, \( \text{sign}\left(\frac{\partial^2 f_{cos}}{\partial v^2}\right)_{x_{ph},v_{ph,1}} = \text{sign}\left(\frac{\partial^2 f_{cos}}{\partial v^2}\right)_{x_{ph},v_{ph,3}} \) due to Equation (5.1e). Since only one real root exists, this root is correctly given by \( v_{ph,1} = v_{ph,3} \) due to Equation (5.1f).

**Three Distinct Real Roots.** In the three-distinct-real-roots region, \( D(x_{ph}) < 0 \) according to Cardano’s method. Then, \( \text{sign}\left(\frac{\partial^2 f_{cos}}{\partial v^2}\right)_{x_{ph},v_{ph,1}} = 1 \neq -1 = \text{sign}\left(\frac{\partial^2 f_{cos}}{\partial v^2}\right)_{x_{ph},v_{ph,3}} \) due to Equation (5.1e), and \( v_{ph,3} < v_{ph,1} \) due to Equation (5.1f) as required. It should be noted that Criterion (5.1) will discriminate between the roots which satisfy the necessary conditions for thermodynamic stability against the root which does not, i.e., it will allow \( v_{ph,1} \) and \( v_{ph,3} \), yet not \( v_{ph,2} \). However, between those two roots, the criterion does not discriminate any further with respect to the sufficient conditions for thermodynamic stability. Consequently, in this case, a criterion such as Problem (5.4) (see Section 5.2.3) is required if the stable state is unknown.

**Three Coinciding Real Roots.** In the case of three coinciding real roots \( D(x_{ph}) = 0 \) according to Cardano’s method. Then, \( \text{sign}\left(\frac{\partial^2 f_{cos}}{\partial v^2}\right)_{x_{ph},v_{ph,1}} \) and \( \text{sign}\left(\frac{\partial^2 f_{cos}}{\partial v^2}\right)_{x_{ph},v_{ph,3}} \) are not determined by Equation (5.1e). Since only one real value is taken, the root is correctly given by \( v_{ph,1} = v_{ph,3} \) due to Equation (5.1f).

**Two Coinciding Real Roots.** In the case of two coinciding real roots \( D(x_{ph}) = 0 \) according to Cardano’s method; however, Criterion (5.1) does not guarantee for \( v_{ph,3} < v_{ph,1} \). Considering that states on the curves 1-2 and 2-3, see Figure 5.4, are far less likely than those in the aforementioned regions, this failure of the criterion might be regarded less relevant. In particular, any state on the line can generally be replaced by a slightly perturbed state in any of the adjacent regions where the criterion works reliably, without considerably affecting, e.g., simulation results. It should be noted that similar reasoning could be applied to the so-called pseudo-critical point 2 in Figure 5.4. The pseudo-critical point is the intersection of the lines \( (\partial f_{cos}/\partial v)_{x_{ph},v_{ph,r}} = 0 \) and \( (\partial^2 f_{cos}/\partial v^2)_{x_{ph},v_{ph,r}} = 0 \), and exhibits three real coinciding roots \([10, 146, 172]\). As, however, all of the three roots coincide at the pseudo-critical point, their discrimination is trivial, and the criterion is fully applicable.

**Thermodynamic Stability**

Having covered all root scenarios, let us recall that Criterion (5.1) satisfies the necessary conditions for thermodynamic stability which follows from [83]. However, it does not satisfy the sufficient conditions for thermodynamic stability, also see Section 5.2.3. Consequently, if the stable state is unknown, a criterion such as Problem (5.4) is required in the case of multiple distinct real roots (see Section 5.2.3). It should be noted that with Equation (5.1f), we consider a particular assignment of root types to variables, e.g., \( v_{ph,3} \) represents liquid and \( v_{ph,1} \) vapor. If we want to consider a different assignment, Equation (5.1f) may
be replaced by
\[ g_{42}(v_{ph,1}, v_{ph,3}) := v_{ph,1} - v_{ph,3} \leq 0. \] (5.3)
See Section 5.2.4 for the application of Criterion (5.1) to case studies in [46].

### 5.2.3 Root Discrimination Based on Thermodynamics

In this section, root discrimination, subject to thermodynamic stability, is discussed by solving a \((P,T)\)-flash problem. [77] solve the flash problem based on Baker’s criterion to global optimality with respect to both mole fraction and molar volume using interval Newton/generalized bisection (IN/GB) methods. Similarly, the flash problem may be solved to global optimality in a reduced variable space using a tunneling method [114, 113]. However, root discrimination is not discussed, nor the fact that the feasible set of roots is to be restricted to physically sensible values. [66] formulate the flash as a minimization problem of the Helmholtz free energy \(\Delta A(x_{ph}, v_{ph,r})\) in the variable molar density, subject to mass balance and a general constraint on volume, as opposed to a cubic equation; the phase and mechanical equilibrium are derived, as well. [112] reformulate the problem in [66] with respect to the Gibbs free energy. The main idea is to express the Gibbs free energy in terms of the Helmholtz free energy such that cubic equality is implicitly met at the stationary point of a problem that minimizes the Gibbs free energy, without imposing cubic equality explicitly as a constraint. The phase and mechanical equilibrium are then derived from the KKT first-order conditions of this problem. Furthermore, Nagarajan and Cullick state that for a given composition, the minimization of the Gibbs free energy with respect to molar volume will result in stationary points of different types; there is a local maximum besides two local minima between which the global minimum jumps. In contrast, according to Nagarajan and Cullick, the Helmholtz free energy with respect to density and volume represents a smooth function. [102] considers the minimization of the Gibbs free energy with respect to volume and molar amounts, and derives the phase and mechanical equilibrium from the KKT first-order conditions.

In contrast, this thesis discusses the KKT first-order conditions of a \((P,T)\)-flash problem in the variables mole fraction, molar volume and phase fraction, as this allows for i) a derivation of a tangent plane criterion based on \(\Delta A(x_{ph}, v_{ph,r})\), ii) a derivation of an alternative formulation in the case of vanishing phases at a noncritical point, and iii) conclusions on root discrimination. We restrict the discussion to two phases and two species, as the higher-dimensional cases are analogous. For simplicity, we consider states that are not critical. Let \(\Delta G(x_{ph}, v_{ph,r})\) denote the molar Gibbs free energy relative to pure species at ideal gas state, and assume that this function is, at least, twice continuously differentiable. For a given feed denoted by \(0\), a stable split at pressure \(P^0 = const\.) and temperature \(T^0 = const\.) is given by the following problem

\[
\begin{align*}
\min_{\Phi, x_{1,I}, v_{1,I}, v_{1,r}, \ldots} & \quad \Phi \Delta G(x_{1,I}, v_{1,r}) + (1 - \Phi) \Delta G(x_{1,II}, v_{1,II,r}) \\
\text{s.t.} & \quad \Phi x_{1,I} + (1 - \Phi) x_{1,II} - x_1^0 = 0 \\
& \quad f_{ceos}(x_{1,I}, v_{1,r}) = 0 \\
& \quad f_{ceos}(x_{1,II}, v_{1,II,r}) = 0 \\
& \quad \Phi \geq 0 \\
& \quad 1 - \Phi \geq 0.
\end{align*}
\] (5.4a-d)
5.2 Thermodynamic Stability and Root Discrimination

It should be noted that phase fraction $\Phi$ may be eliminated in the objective with the help of Equation (5.4b). However, this equality constraint (EC) implies some important intermediate results which will be discussed in Section 5.2.3. For a single-phase solution $\Phi \in \{0, 1\}$, while for a two-phase solution $\Phi \in (0, 1)$. In the general case of mixtures, the number of phases is not to be confused with the number of real roots in the ECs (5.4c) and (5.4d) [69, 141].

If the feasible set contains two or three distinct real roots $v_{ph,r}$ for a given $x_{ph}$, a global solution of Problem (5.4) will discriminate between the roots according to thermodynamic stability. In the trivial case of the feasible set containing a single real root or three coinciding real roots $v_{ph,r}$ for a given $x_{ph}$, discrimination is not required and $v_{ph,r}$ will be the stable root according to Problem (5.4). It should be noted that feasibility of Problem (5.4) is guaranteed since there exists, at least, one real root to a cubic equation. See Section 5.2.4 for an application of Problem (5.4) to case studies in [46].

Statement of Reformulated Flash Problem

In order to eliminate the cubic ECs, Problem (5.4) may be rewritten using the formulation in [112]. Assuming that $\Delta A(x_{ph}, v_{ph,r})$ is, at least, twice continuously differentiable, Problem (5.4) reads

$$\begin{align*}
\min_{\Phi, x_{1, II}, v_{1, r}, v_{II, r}} & \quad \Phi \left( \Delta A(x_{1, I, v_{1, r}}) + P^0 v_{1, r} \right) \\
& \quad + (1 - \Phi) \left( \Delta A(x_{1, II, v_{II, r}}) + P^0 v_{II, r} \right) \\
\text{s.t.} & \quad \Phi x_{1, I} + (1 - \Phi) x_{1, II} - x^0_1 = 0 \\
& \quad \Phi \geq 0 \quad \text{(5.5b)} \\
& \quad 1 - \Phi \geq 0 \quad \text{(5.5d)}
\end{align*}$$

In Appendix H.1, we discuss the KKT first-order conditions to show that Problem (5.5) and thus, also Problem (5.4) gives a stationary point that satisfies the necessary conditions for thermodynamic stability. In the following, we will summarize our results.

Implications of KKT Conditions

In this paragraph, some implications of the KKT first-order conditions of Problem (5.5) are discussed: $i)$ a tangent plane criterion in terms of $\Delta A(x_{ph}, v_{ph,r})$, $ii)$ a proposed formulation in the case of vanishing phases at a noncritical point, and finally, $iii)$ a necessary condition for stability of the selected root.

Regarding $i)$, [82] mention a tangent criterion for pure species. [66] derive a tangent plane criterion for the Helmholtz free energy from the KKT first-order conditions for the minimization in the variable molar density, and show the relation to the convex hull of the Helmholtz free energy. [112] extend their work and prove the tangent plane distance criterion for the Helmholtz free energy with respect to density and volume. Finally, [128] derive a tangent plane criterion for $\Delta A(x_{ph}, v_{ph,r})$ with respect to mole fraction and volume using a dual problem formulation [106]. For the well-known tangent plane criterion with respect to $\Delta G(x_{ph})$, see [12]. In contrast, in Appendix H.1, a tangent plane criterion in terms of $\Delta A(x_{ph}, v_{ph,r})$ in the variables mole fraction, phase fraction and molar volume is derived from the KKT first-order conditions of a simple $(P, T)$-flash (Problem (5.5)) with
both phases present. The corresponding tangent plane is given by

\[
\Delta A(x_{1,\text{II}}, v_{\text{II},r}) - \Delta A(x_{1,\text{I}}, v_{\text{I},r}) = \left( \frac{\partial \Delta A}{\partial x} \right)_{x_{1,\text{I}},v_{\text{I},r}} (x_{1,\text{II}} - x_{1,\text{I}}) + \left( \frac{\partial \Delta A}{\partial v} \right)_{x_{1,\text{I}},v_{\text{I},r}} (v_{\text{II},r} - v_{\text{I},r}).
\]

(5.6)

The criterion implies that a stationary point of Problem (5.5) satisfies cubic equality, isopotential and mechanical equilibrium with the latter being necessary for thermodynamic stability.

If a phase vanishes, it is proposed (ii) not to impose a root for the phase that does not exist, in Appendix H.1. [65] and the corresponding follow-up [18] formulate the minimization of the Gibbs free energy in the space of molar amounts, and [145] formulate in the space of molar amounts and mole fractions. These works discuss the KKT first-order conditions for the Gibbs free energy minimization, in order to derive that isopotential is relaxed in case a phase vanishes which is, however, only one of two major implications of a vanishing phase in terms of CEOS. In the variable space of Problem (5.5), a result equivalent to the one from the literature is given by

\[
0 \leq \left( \left( \frac{\partial \Delta A}{\partial x} \right)_{x_{1,\text{I}},v_{\text{I},r}} + \lambda_1 \right) \perp \Phi \geq 0.
\]

(5.7)

It should be noted that Equation (5.7) encodes a complementarity condition, i.e., either the bracketed term or \( \Phi \) or both are equal to zero, and both are greater equal zero. In terms of the second major implication of a vanishing phase, it is shown in Appendix H.1 that

\[
0 \leq \left( -P \right)_{x_{1,\text{I}},v_{\text{I},r}} + P^0 \perp \Phi \geq 0,
\]

(5.8)

i.e., also cubic equality and hence, mechanical equilibrium may be relaxed if a phase vanishes. In fact, relaxation of isopotential, cubic equality and mechanical equilibrium are coupled through their joint dependence on \( \Phi \). That is, cubic equality, along with phase and mechanical equilibrium, are all relaxed simultaneously if a phase vanishes. As a result, the relaxation of cubic equality is a viable alternative to the relaxation of root discrimination criteria. The concept of relaxing pressure is also discussed in [27], yet without this direct relation to the KKT conditions.

Finally, let us consider (iii), noting that from the tangent plane criterion, an intermediate result on root discrimination may be obtained. Since there is a supporting tangent plane, \( \Delta A(x_{ph}, v_{ph,r}) \) is locally convex with respect to both composition and molar volume, i.e.,

\[
\left( \frac{\partial^2 \Delta A}{\partial x^2} \right)_{x_{1,\text{I}},v_{\text{I},r}} \geq 0
\]

(5.9a)

\[
\left( \frac{\partial^2 \Delta A}{\partial v^2} \right)_{x_{1,\text{I}},v_{\text{I},r}} = - \left( \frac{\partial P}{\partial v} \right)_{x_{1,\text{I}},v_{\text{I},r}} \geq 0
\]

(5.9b)

\[
\left( \frac{\partial^2 \Delta A}{\partial x^2} \right)_{x_{1,\text{II}},v_{\text{II},r}} \geq 0
\]

(5.9c)

\[
\left( \frac{\partial^2 \Delta A}{\partial v^2} \right)_{x_{1,\text{II}},v_{\text{II},r}} = - \left( \frac{\partial P}{\partial v} \right)_{x_{1,\text{II}},v_{\text{II},r}} \geq 0.
\]

(5.9d)
Table 5.1: Binary interaction parameters $k_{12}$ for PR taken from Aspen DRS [8].

<table>
<thead>
<tr>
<th>Species</th>
<th>CO$_2$</th>
<th>Ar</th>
<th>O$_2$</th>
<th>N$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-0.017</td>
</tr>
<tr>
<td>Ar</td>
<td>0</td>
<td>0</td>
<td>0.0104</td>
<td>-0.0026</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0</td>
<td>0.0104</td>
<td>0</td>
<td>-0.0119</td>
</tr>
<tr>
<td>N$_2$</td>
<td>-0.017</td>
<td>-0.0026</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

In particular, Equations (5.9b) and (5.9d) are the well-known condition for mechanical stability, see e.g., [162], and can, thus, be applied to discriminate the intermediate root to a CEOS against the maximum and the minimum root, in case the CEOS gives three distinct real roots, see e.g., [83]. As a consequence, Equations (5.9b) and (5.9d) are a necessary condition for thermodynamic stability of the selected root.

Altogether, three results are obtained from the KKT first-order conditions. These are: 
i) There exists a tangent plane criterion $\Delta A(x_{ph},v_{ph,r})$. 
ii) Relaxing cubic equality is an alternative to relaxing root discrimination criteria, in order to capture vanishing and reappearing phases. 
iii) Equations (5.9b) and (5.9d) are a necessary condition for stability of a root and should, thus, be considered when formulating root discrimination criteria.

5.2.4 Analysis and Application to Case Studies

In Section 5.2.1, root discrimination criteria from the literature are listed. In the present section, the objections in [46] to the particular criterion in [83], as well as the modifications proposed in [46] are discussed. In our discussion, special attention is paid to thermodynamic stability, by comparing the modified criterion in [46] to Problem (5.4) and Criterion (5.1). In Appendices H.2.1 to H.2.3, further root discrimination criteria from the literature are discussed.

Computational Details

We use a 64-bit processor 3.30 GHz running Windows 7, and the global solver BARON [161] 16.3.4 with the settings: AbsConFeasTol 1e-5, RelConFeasTol 0.0, NlpSol -1, LpSol 3, NodeSel 1, NOuter1 8, NOutIter 8, NOutPerVar 8, PDm -1. For the optimality tolerances we set optca and optcr to 1e-4 in most cases, and to 1e-5 only if it is clear from the results that the global minimum is not yet achieved for a greater optimality gap. For the results in the present section, the same equations and parameters are implemented for PR, for the same mixture as used in [46], comprising 97 mol% CO$_2$, 1 mol% Ar, 1 mol% O$_2$, 1 mol% N$_2$, and 50 mol% CO$_2$, 50 mol% N$_2$, respectively. We reformulate some of the equations, in order to accelerate/enable convergence of BARON. For big-M, we choose 1000, as this allows for the required relaxations, while at the same time not excluding valid points. The complementarity condition in Problem (5.11) is regularized according to $s_1 \cdot \Phi \leq \epsilon, s_2 \cdot (1 - \Phi) \leq \epsilon$, where $\epsilon = 1e-6$. Critical data and binary interaction coefficients are taken from Aspen DRS [8] because those are not reported in the respective works; the latter are given in Table 5.1. If the interaction coefficients are not given, they are assumed zero. Although there is no thermodynamic indication of these values being zero, it is common practice and the results do not suggest otherwise, especially since we can
confirm some of the results from the literature; thus, we will follow this simplification in this thesis.

Analysis of the Criterion of Dowling et al.

[46] discuss the criterion in [83] and extend it. For a mixture of 97 mol% CO$_2$/1 mol% Ar/1 mol% N$_2$/1 mol% O$_2$, they calculate the phase envelope (without stating how) and the lines $(d f_{ceos}/d Z)|_{x_{ph},Z_{ph, r}} = 0$ and $(d^2 f_{ceos}/d Z^2)|_{x_{ph},Z_{ph, r}} = 0$ of the criterion in [83], in order to demonstrate its weaknesses. [46, Sections 2.2.2 to 2.2.5] motivate the need for a modification, address the shortcomings of the criterion, and conclude with a summary of the modified model. In total, we identify three points that the authors criticize on the criterion, as follows:

Objection 1. According to [46] the criterion assigns incorrect phase types outside the three-real-root region. In particular, the criterion predicts a phase transition from liquid to vapor for isothermal compression at 200 K [46, Figure 2]. We would like to point out that the respective state, by itself, is sub-critical but the modification of the criterion is discussed with respect to super-critical states. In particular, it is proposed to further relax the root discrimination constraints in such a way that the roots are not discriminated in the super-critical region.

Objection 2. [46, Figure 2] state “This point is below the dew point curve, and thus must be only a vapor. However, this point is also in the three-root region and a liquid root for $Z$ exists at this point. Thus (8) and (9) [relaxed equations of the criterion] are necessary but not sufficient for predicting the proper number of phases. Additional information, such as component fugacities, must also be considered.” We interpret this statement as follows: In the single-phase region, the criterion will fail if it is applied to more than one real root.

Objection 3. [46, Section 2.2.4] discuss nonphysical single-phase solutions in the two-phase region, and argue that this is due to the fact that the formulation uses only a necessary condition for thermodynamic stability. They also seem to observe $\text{sign} \left( \frac{\partial f_{ceos}}{\partial Z^2} \right)_{x_{I},Z_{I,3}} = \text{sign} \left( \frac{\partial^2 f_{ceos}}{\partial Z^2} \right)_{x_{III},Z_{III,3}}$ for these solutions. We have comparable findings for the VLE of CO$_2$/N$_2$, as will be discussed shortly.

For an illustrative argumentation, we apply Problem (5.4) and Criterion (5.1) to the mixture given in [46] for different states $(P, T)$ using BARON [161]. It should be noted that Problem (5.4) is essentially [46, Problem (16)], yet without the complementarity condition.

Besides the aforementioned Objections 1 to 3, we observe a special property in [46, Figure 2]. Interestingly, it depicts a two-phase region that is a subset of the region of three distinct real roots which is a rather specific behavior; see e.g., [141, Figure 8-17] for a counterexample where the single-real-root region and the two-phase region intersect. An issue resulting from this behavior is related to the definition of the critical point for mixtures. This is the point of intersection of bubble and dew point curve; the critical isotherm of a CEOS may yield up to three distinct real roots at this point [75]. In contrast, the pseudo-critical point
5.2 Thermodynamic Stability and Root Discrimination

Table 5.2: Results of Problem (5.4) and Criterion (5.1) at 200 K and $1 \times 10^7 \text{N m}^{-2}$, for a feed consisting of 97 mol\% CO$_2$, 1 mol\% Ar, 1 mol\% O$_2$, 1 mol\% N$_2$. $\Phi = 1$ indicates that the stable state is single-phase, and since the stable state according to Problem (5.4) satisfies $(\frac{\partial^2 f_{\text{cos}}}{\partial Z^2})_{x_{\text{ph}},Z_{\text{ph}},3} \leq 0$, the phase is liquid following [83]. Criterion (5.1) is in agreement with Problem (5.4). Since from Criterion (5.1) the same state is found for both root variables, only one real root exists.

<table>
<thead>
<tr>
<th>Label</th>
<th>Problem (5.4)</th>
<th>Criterion (5.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase 1</td>
<td>Phase 2</td>
</tr>
<tr>
<td>$\Phi_j$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$(\frac{\partial f_{\text{cos}}}{\partial Z})<em>{x</em>{\text{ph}},Z_{\text{ph}},3}$</td>
<td>1.1746</td>
<td>n. appl.</td>
</tr>
<tr>
<td>$(\frac{\partial^2 f_{\text{cos}}}{\partial Z^2})<em>{x</em>{\text{ph}},Z_{\text{ph}},3}$</td>
<td>-0.46929</td>
<td>n. appl.</td>
</tr>
<tr>
<td>$D(x_{\text{ph}})$</td>
<td>n. appl.</td>
<td>n. appl.</td>
</tr>
<tr>
<td>UBD</td>
<td>-3.6082</td>
<td>-3.6082</td>
</tr>
<tr>
<td>LBD</td>
<td>-3.6086</td>
<td>-3.6086</td>
</tr>
<tr>
<td>CPU time</td>
<td>128 s</td>
<td>156 s</td>
</tr>
</tbody>
</table>

exhibits three real coinciding roots [10, 146, 172], also see Figure 5.4. Although the pseudocritical point does not necessarily coincide with the true critical point, the agreement is surprisingly good [46, Figure 2].

Objection 1: Results and Discussion. [46, Equations (11c), (11d)] state that the criterion in [83] assigns incorrect phase types outside the three-real-root region. We can confirm their observations, see Tables 5.2 and 5.3. The tables should be read as follows: When $\Phi = 0$, roots and discriminant $D(x_{\text{ph}})$ cannot be reported, as the corresponding phase does not exist. When $\Phi \in (0, 1]$, however, Problem (5.4) will yield only that root which satisfies the sufficient condition for thermodynamic stability. In contrast, Criterion (5.1) will report all those roots that satisfy the necessary condition for thermodynamic stability according to Equations (5.9b) and (5.9d), in addition to discriminant $D(x_{\text{ph}})$. $D(x_{\text{ph}}) < 0$ indicates two distinct real roots satisfying the necessary condition, whereas for $D(x_{\text{ph}}) > 0$, there exists only one real root and the root variables will coincide according to Criterion (5.1). It should be noted that we use PR CEOS to check the results from [46], while it is not clear which CEOS model is used for their objections. The results in Tables 5.2 and 5.3 indicate that there exists a single phase and that the CEOS yields only one real root. This is in agreement with the observations in [46] for this sub-critical state. Since [46] also discuss super-critical states we would like to add, as an aside, that there are specific cases of mixture behavior in the super-critical region: If the pure species are sufficiently different in terms of, e.g., polarity and molecular shape, the critical loci may be discontinuous and phenomena such as gas-gas phase splits and three-phase equilibria may occur [172].
5 Parameter Estimation of Cubic Equations of State (CEOS)

Table 5.3: Results of Problem (5.4) and Criterion (5.1) at 200 K and $1.5 \times 10^7$ N m$^{-2}$, for a feed consisting of 97 mol% CO$_2$, 1 mol% Ar, 1 mol% O$_2$, 1 mol% N$_2$. $\Phi = 1$ indicates that the stable state is single-phase, and since the stable state according to Problem (5.4) satisfies $(\partial^2 f_{\text{ceos}}/\partial Z^2)|_{x_{I},Z_{I},1} \geq 0$, the phase is vapor following [83]. Criterion (5.1) is in agreement with Problem (5.4). Since from Criterion (5.1) the same state is found for both root variables, only one real root exists.

<table>
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<th>Criterion (5.1)</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Phase 1</td>
<td>Phase 2</td>
</tr>
<tr>
<td>$\Phi_j$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$(\frac{\partial f_{\text{ceos}}}{\partial Z})</td>
<td><em>{x</em>{ph},Z_{ph},1}$</td>
<td>1.8444</td>
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<tr>
<td>$(\frac{\partial^2 f_{\text{ceos}}}{\partial Z^2})</td>
<td><em>{x</em>{ph},Z_{ph},1}$</td>
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<td>$(\frac{\partial f_{\text{ceos}}}{\partial Z})</td>
<td><em>{x</em>{ph},Z_{ph},3}$</td>
<td>n. appl.</td>
</tr>
<tr>
<td>$(\frac{\partial^2 f_{\text{ceos}}}{\partial Z^2})</td>
<td><em>{x</em>{ph},Z_{ph},3}$</td>
<td>n. appl.</td>
</tr>
<tr>
<td>$D(x_{ph})$</td>
<td>n. appl.</td>
<td>n. appl.</td>
</tr>
<tr>
<td>UBD</td>
<td>-3.9130</td>
<td>-3.9130</td>
</tr>
<tr>
<td>LBD</td>
<td>-3.9134</td>
<td>-3.9134</td>
</tr>
<tr>
<td>CPU time</td>
<td>122 s</td>
<td>260 s</td>
</tr>
</tbody>
</table>

Objection 2: Results and Discussion. We can confirm the observation in [46] that at 250 K and $1.5 \times 10^7$ N m$^{-2}$, the criterion predicts a single vapor phase, and that the CEOS yields, at least, two real roots of which only the vapor root is stable, see Table 5.4. However, from this finding, we cannot draw the same conclusion as [46]. The reason for this is that for mixtures, the number of real roots to the CEOS is not to be confused with the number of phases [69] which may be determined by Gibbs’ phase rule, under suitable assumptions. Let us consider now the case of the CEOS giving three real roots at state $(P,T)$ at which only one phase exists. [141, Figure 8-17] give a $(P,T)$-diagram like, e.g., Figure 5.4, for 26.54% ethane and 73.46% n-heptane modeled with the Soave CEOS. It illustrates that neither three-real-root nor two-phase region necessarily are a subset of each other. Consequently, this is a counterexample of the statement that the three-real-root region includes the two-phase region as a subset. Similarly, [136] point out that the three-real-root region may we wider or narrower than the two-phase region. Consequently, the criticism in [46] on the criterion in [83] is not justified in our opinion.

Objection 3: Results and Discussion. [46] mention nonphysical single-phase solutions in the two-phase region, in particular they seem to observe

$$\text{sign} \left( \frac{\partial^2 f_{\text{ceos}}}{\partial Z^2} \right)|_{x_{I1},Z_{I1},1} = \text{sign} \left( \frac{\partial^2 f_{\text{ceos}}}{\partial Z^2} \right)|_{x_{I2},Z_{I2},3}. \quad (5.10)$$

In [46], it is argued that the solutions are nonphysical due to the fact that only a necessary condition for stability (isopotential) is applied. In order to exclude these erroneous solutions, the necessary condition is not replaced by a sufficient condition, presumably because this would result in an embedded problem in their case. Instead, they add constraints on temperature [46, Equation (17)]. We seem to have similar findings for the VLE of CO$_2$/N$_2$. 

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5.2 Thermodynamic Stability and Root Discrimination

Table 5.4: Results of Problem (5.4) and Criterion (5.1) at 250 K and $1.5 \times 10^6 \text{ N m}^{-2}$, for a feed consisting of 97 mol% CO$_2$, 1 mol% Ar, 1 mol% O$_2$, 1 mol% N$_2$. $\Phi = 1$ indicates that the stable state is single-phase, and since the stable state according to Problem (5.4) satisfies $(\partial^2 f_{\text{cos}}/\partial Z^2)_{x_1,z_{1,1}} \geq 0$, the phase is vapor following [83]. From Criterion (5.1) the same state is correctly identified, in addition to the third root which satisfies only the necessary, yet not the sufficient condition for stability. Since $(\partial^2 f_{\text{cos}}/\partial Z^2)_{x_1,z_{1,3}} \leq 0$ for this root, it is liquid-like according to [83].

<table>
<thead>
<tr>
<th>Label</th>
<th>Problem (5.4)</th>
<th>Criterion (5.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase 1</td>
<td>Phase 2</td>
</tr>
<tr>
<td>$\Phi_j$</td>
<td>1</td>
<td>0</td>
</tr>
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<td>$(\partial f_{\text{cos}}/\partial Z)<em>{x</em>{ph, z_{ph,1}}}$</td>
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<td>n. appl.</td>
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<tr>
<td>$(\partial^2 f_{\text{cos}}/\partial Z^2)<em>{x</em>{ph, z_{ph,3}}}$</td>
<td>n. appl.</td>
<td>n. appl.</td>
</tr>
<tr>
<td>$D(x_{ph})$</td>
<td>n. appl.</td>
<td>n. appl.</td>
</tr>
<tr>
<td>UBD</td>
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</tr>
<tr>
<td>LBD</td>
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<tr>
<td>CPU time</td>
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<td>202 s</td>
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</tbody>
</table>

which is a binary subsystem of the quaternary system examined in [46]. At 250 K and $1.4066 \times 10^7 \text{ N m}^{-2}$ measurements of, e.g., [157], indicate that CO$_2$/N$_2$ exhibits a VLE. In order to examine the binary system, we use the compressibility factor $Z_{ph,r}$ and solve Problem (5.4), subject to

\[
\left. \left( \frac{\partial f_{\text{cos}}}{\partial Z} \right) \right|_{x_1,z_{1,r}} \geq 0 
\]

\[
\left. \left( \frac{\partial f_{\text{cos}}}{\partial Z} \right) \right|_{x_{II},z_{II,r}} \geq 0 \quad (5.11b)
\]

\[
\left. \left( \frac{\partial^2 f_{\text{cos}}}{\partial Z^2} \right) \right|_{x_1,z_{1,r}} \geq -M_i \cdot s_1 
\]

\[
\left. \left( \frac{\partial^2 f_{\text{cos}}}{\partial Z^2} \right) \right|_{x_{II},z_{II,r}} \leq M_i \cdot s_2 
\]

\[
0 \leq \Phi \perp s_1 \geq 0 
\]

\[
0 \leq (1 - \Phi) \perp s_2 \geq 0, \quad (5.11f)
\]

which is altogether denoted by Problem (5.11). As this represents the formulation in [83, Equations (29), (30), (41), (42)] and [46, Equations (11c), (11d), (6i), (6j)], respectively, but with the necessary condition for stability (isopotential) replaced by the sufficient one (minimization of the Gibbs free energy), the reason for nonphysical roots according to [46] should be excluded. However, the LBD of Problem (5.11) is worse than the UBD of Problem (5.4), cf. Table 5.5 and thus, even Problem (5.11) does not give a stable state. It should be noted that the results of Problem (5.11) in Table 5.5 are close to the nonphysical
Table 5.5: Results of Problem (5.4), Criterion (5.1) and Problem (5.11) at 250 K and 1.4066 \times 10^7 \text{N m}^{-2}, for a feed consisting of 50 mol\% CO\textsubscript{2}, 50 mol\% N\textsubscript{2}. Problem (5.11) gives a worse LBD than the UBD of Problem (5.4) and hence, not a stable state. Criterion (5.1) agrees with Problem (5.4) within optcr 1e-4 and optca 1e-4, respectively.

<table>
<thead>
<tr>
<th>Label</th>
<th>Problem (5.11)</th>
<th>Problem (5.4)</th>
<th>Criterion (5.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase 1</td>
<td>Phase 2</td>
<td>Phase 1</td>
</tr>
<tr>
<td>(\Phi_j)</td>
<td>0.9927</td>
<td>0.0073</td>
<td>0.293</td>
</tr>
<tr>
<td>(\left(\frac{\partial^2 f_{\text{eos}}}{\partial Z^2}\right)<em>{x</em>{ph},Z_{ph},1})</td>
<td>1.3625</td>
<td>0.13639</td>
<td>0.2829</td>
</tr>
<tr>
<td>(\left(\frac{\partial^2 f_{\text{eos}}}{\partial Z^2}\right)<em>{x</em>{ph},Z_{ph},3})</td>
<td>1.3625</td>
<td>0.13639</td>
<td>0.2829</td>
</tr>
<tr>
<td>(s)</td>
<td>10(^{-6})</td>
<td>1.4 \times 10^{-4}</td>
<td>n. appl.</td>
</tr>
<tr>
<td>(D(x_{ph}))</td>
<td>n. appl.</td>
<td>n. appl.</td>
<td>n. appl.</td>
</tr>
<tr>
<td>UBD</td>
<td>-1.32869</td>
<td>-1.33149</td>
<td>-1.33152</td>
</tr>
<tr>
<td>LBD</td>
<td>-1.32882</td>
<td>-1.33163</td>
<td>-1.33166</td>
</tr>
<tr>
<td>CPU time</td>
<td>57 s</td>
<td>847 s</td>
<td>1082 s</td>
</tr>
</tbody>
</table>

single-phase solutions with the same root types as [46] seem to have observed, i.e., \(\Phi = 0.9927 \approx 1\) together with Equation (5.10). The results in Table 5.5 are not exactly single-phase (\(\Phi = 1\)) due to our particular choice of big-\(M\) and \(\epsilon\). However, for different settings we observed a bad scaling of the problem.

It follows that erroneous solutions of the formulation from the literature are not necessarily due to the lack of the sufficient conditions. Instead, these may be caused by incorrect root discrimination, Equations (5.11c) to (5.11f). The reason for this is that for the state under consideration, there exist only the same root types, i.e.,

\[
\left(\frac{\partial^2 f_{\text{eos}}}{\partial Z^2}\right)_{x_{ph},Z_{ph},1} > 0, \forall r \quad (5.12a)
\]

\[
\left(\frac{\partial^2 f_{\text{eos}}}{\partial Z^2}\right)_{x_{ph},Z_{ph},3} > 0, \forall r \quad (5.12b)
\]

and this is not considered by Equations (5.11c) and (5.11d). Since the only existent root is of a type given in Equation (5.12b), it follows \(s_2 > 0\) according to Equation (5.11d), and \(\Phi = 1\) according to Equation (5.11f). Consequently, the formulation from the literature risks to exclude potentially valid solutions for single real roots.

In order to consider the single-real-root case, revisions of Equations (5.11c) and (5.11d) are required. [46, Equations (11c) and (11d)] seem to suggest such a revision. These imply a relaxation in the super-critical region which in their particular case coincides with the problematic region of single-real roots. However, this coincidence is a very specific behavior of the examined fluid system, and does not generally occur [143, p. 197]. Consequently, the relaxation of Equations (5.11c) and (5.11d) should not be related to the super-critical region (thermodynamics) as suggested in [46], but to the single-real-root region (calculus of cubic equations) as considered in, e.g., Criterion (5.1). As a reference, we also report the results of Criterion (5.1) which agree with those of Problem (5.4) within optca and optcr as required. It should be noted that in the single-real-root region, Criterion (5.1) does not exclude candidate solutions, however, at the cost of CQs, see Appendix I. Furthermore,
5.2 Thermodynamic Stability and Root Discrimination

Fig. 5.5: Illustration of Table 5.5, VLE of CO₂/N₂ at 250.0 K and 1.4066 × 10⁷ N m⁻². Upper left: Reduced molar Gibbs free energy as a function of mole fraction x. Only one Gibbs free energy branch exists, indicating that either only one real solution to the CEOS exists, or that the solutions coincide. Upper right: “Root 1” denotes the case in the LHS figure. ∆G(x_{ph}, v_{ph,1}) < ∆G(x_{ph}, v_{ph,3}), ∀x_{ph} ∈ (0, 1). For feeds x_{0}^{0.1} and x_{0}^{0.2} (straight vertical lines), in the stable state, there are two phases of compositions x_I and x_{II}, respectively (dot-dashed lines), both root 1. For feed x_{0}^{0.1}, Problem (5.11) gives incorrect compositions x_I and x_{II}, respectively (dotted lines), and for feed x_{0}^{0.2}, it erroneously results in a single phase. Bottom: Schematics of consequences for process simulation. Bottom left: Criterion (5.1) correctly gives a VLE. Bottom right: Problem (5.11) erroneously gives a single-phase vapor state.

the aforementioned reasoning, generally, is not extensible to pure species. For these, the pseudo-critical and the critical point predicted by the CEOS coincide and thus, commonly, all required root types will exist in the two-phase region.

For a graphical interpretation of the results in Table 5.5, see Figure 5.5. Applying Baker’s criterion [12] to the minimization of the Gibbs free energy, subject to root discrimination, the supporting tangent plane must not be excluded from the feasible region. For a feed x_{0} ∈ (x_{II}, x_I), Problem (5.4) and Criterion (5.1) correctly result in the stable state of two phases. In contrast, root discrimination, such as [83], will erroneously result in a single phase. The reason for this is that different root types are imposed, while only one exists. As this will not give the stable state, we conclude that the root discrimination from the literature is too restrictive.

Objections 1 to 3: Summary. We can confirm the objections in [46] to the criterion in [83] in parts. However, we cannot follow the argumentation on the relation between the number of phases and the number of roots, nor on the causes of nonphysical solutions.
Their measures undertaken to improve the criterion are based on thermodynamics but, in our opinion, should be based on the calculus of cubic equations. In addition, we would like to point out that the formulations [46, 83] may exclude potentially valid solutions. In contrast, with Criterion (5.1) correct results are obtained as demonstrated in Tables 5.2, 5.3 and 5.5. It should be noted that these results are not affected by violation of CQs, also see Section 5.2.2.

Although the example from Table 5.5 is rather specific, as it represents a state which is not too far off the critical point, the case of incorrect root discrimination is of practical importance in our opinion. The reason for this is that incorrect discrimination as reported in this section is caused by a weakness which is of methodological nature and, as such, not restricted to the fluid system, nor to the type of equation of state under consideration, or to initial values within potential process simulation studies. In contrast, there is a risk of incorrect root discrimination whenever the stable state according to Problem (5.4) is in the two-phase region of the VLE and at the same time in the single-real-root region, also see Figure 5.4. We recommend the reader to check respective calculation results should these be based on [83, Equations (29), (30), (41), (42)], as to date, there is no indication that two-phase and single-real-root region should not overlap in the majority of the cases in, e.g., process simulation or optimization.

5.2.5 Interim Conclusions

A root discrimination criterion is proposed that is based on the calculus of cubic equations, in particular the well-known method of Cardano: Criterion (5.1) is straightforward, continuous and covers different root scenarios. As a reference criterion, the minimization of the Gibbs free energy is formulated in form of a \((P,T)\)-flash, see Problem (5.4). From the KKT first-order conditions of Problem (5.4), we conclude that the relaxation of cubic equality is an alternative to relaxation of root discrimination constraints in case a phase vanishes. In a literature review, several root discrimination criteria are compared to Criterion (5.1) and Problem (5.4). It is found that only Problem (5.4) uses a sufficient condition for thermodynamic stability of the selected root, whereas Criterion (5.1) and those from the literature satisfy, at best, a necessary condition for stability. Moreover, in certain root scenarios, the formulations in [83] and [46] are found to exclude valid solutions, while Criterion (5.1) does not exhibit this deficiency, as demonstrated with the case study \(\text{CO}_2/\text{N}_2\). Although it is shown that the latter criterion theoretically violates the most common constraint qualifications under certain conditions, this does not affect the results in practice, as the agreement between the results obtained for case studies from natural gas reservoirs and the literature suggests. In the following section, we propose a bilevel program for parameter estimation of CEOS models, based on this root discrimination criterion.

5.3 Review of Problem Formulations

In this section, a BLP for parameter estimation of CEOS, subject to necessary and sufficient criteria for thermodynamic stability is proposed, motivated by the need for preventing the erroneous behavior of a process simulator reported in Section 5.1. We will first review the standard (single-level) formulation that may cause this undesired behavior, alongside two examples of basic approaches from the literature which can be interpreted as early
BLPs.

5.3.1 Standard Formulation

Let \( f(\cdot) \) denote an objective function indicating the goodness of fit. Although the method allows arbitrarily many experiments, for the sake of notational simplicity, let us assume a regression for a single measurement tuple at \( T, P = const. \), and the case of multiple tuples is analogous. Then, the formulation based on the necessary stability criteria only is given by Problem (5.13)

\[
\min_{x, v_1, v_3, q} f(x, v_1, v_3, q)
\]

s.t. \( \varphi_{i,1} (v_{1, r_1}, x_1, q) \cdot x_{i,1} = \varphi_{i, ph} (v_{ph, r_3}, x_{ph}, q) \cdot x_{i,ph}, \)
\[
\forall ph = \Pi, \ldots, P_h, \forall i = 1, \ldots, N - 1
\]

\( \varphi_{N,1} (v_{1, r_1}, x_1, q) \cdot \left( 1 - \sum_{i=1}^{N-1} x_{i,1} \right) = \varphi_{N, ph} (v_{ph, r_3}, x_{ph}, q) \cdot \left( 1 - \sum_{i=1}^{N-1} x_{i,ph} \right), \)
\[
\forall ph = \Pi, \ldots, P_h
\]

\( f_{cos} (x, v_r, q) = 0, \forall r \in \{1, 3\} \)

\( g (x, v_1, v_3, q) \geq 0 \)

\( \ldots \),

where \( q \) denotes the parameter vector, \( x_{i,ph} \) and \( \varphi_{i,ph} \) the mole fraction and fugacity coefficient, respectively, of species \( i \) in phase \( ph \), and \( N \) the total number of species in the system. Equation (5.13c) represents the CEOS \( \forall ph \) and Equation (5.13d) a certain root discrimination criterion comprising inequality constraints (ICs), cf. Section 5.2. The number of single equations representing Equation (5.13c) and thus, the number of volume variables \( v_r \) depends on the aforementioned criterion. Besides, Problem (5.13) may also include constraints on local convexity of \( \Delta G_{ph} (x_{ph}, \cdot) \) in \( x_{ph} \), which is a common necessary criterion for stability. Similarly, Equations (5.13a) and (5.13b) represent the well-known isopotential criterion. Problem (5.13) considers, thus, only the necessary, yet not the sufficient criteria for thermodynamic stability. This may be interpreted graphically as constraining \( x_{ph} \) to lie on the same tangent to \( \Delta G_{ph} (x_{ph}, \cdot) \) (cf. Figure 2.1, [12]). Consequently, Problem (5.13) does not prevent \( q \) from resulting in violations of Baker’s criterion or from giving spurious phase splits or phases as reported in Section 5.1. In Section 5.4, a rigorous bilevel formulation is proposed to overcome these issues.

5.3.2 Early Bilevel Programs

[148] and the follow-up [47, 48] are mentioned as early examples of bilevel programming in parameter estimation of CEOS at the beginning of this chapter. In this section, we will focus on the formulations proposed in their works, and contrast them to this thesis. In order to avoid spurious LLE when regressing VLE data, [148] impose

\[
\begin{align*}
\min_{x_{l, ph} \in X_{l, ph}} & \quad \left( \frac{\partial^2 \Delta G_{\text{liquid}}}{\partial x_{l, ph}^2} \right)_{x_{l, ph}} \\
\end{align*}
\]

\( > 0 \)
as constraints on the minimization of the model-experiment mismatch, cf. Figure 2.1c. This yields in essence, a BLP for parameter estimation. [148] do not elaborate on the implementation of this challenging problem type, including the specification of host set \( X^{l,lp,S} \). [47] seem to use the thermodynamic reference state “pure ideal gas” and reformulate Equation (5.14) to

\[
\left( \frac{\partial \ln (\phi_{i,\text{liquid}})}{\partial x_{\text{liquid}}} \cdot \frac{P}{P_{\text{id.gas}}} \right) \mid_{X^{l,lp}} > 0,
\]

\( \forall x^{l,lp} \in (0, 1)^{n_{x,lp}} \), \( i = 1, \ldots, N - 1 \). (5.15)

This gives a Semi-Infinite Program (SIP) for parameter estimation with SIP-Slater points, i.e., strict convexity of \( \Delta G_{\text{liquid}}(x_{\text{ph}}, \cdot) \) everywhere. [47] seem to finally, implement a relaxed version of Equation (5.15) given by

\[
\left( \frac{\partial \ln (\phi_{i,\text{liquid}})}{\partial x_{\text{liquid}}} \cdot \frac{P}{P_{\text{id.gas}}} \right) \mid_{X^{n,lp}} > 0 \quad \text{(5.16a)}
\]

\[
x^{n,lp} \in \arg \min_{x^{l,lp} \in X^{l,lp,E}} \left( \frac{\partial \ln (\phi_{i,\text{liquid}})}{\partial x_{\text{liquid}}} \cdot \frac{P}{P_{\text{id.gas}}} \right) \mid_{X^{l,lp}}, \quad \forall i = 1, \ldots, N - 1, \quad \text{(5.16b)}
\]

where \( X^{l,lp,E} \) is a discrete set of measurements. [47] embed Equation (5.16) in the minimization of the model-experiment mismatch which results in a BLP for parameter estimation. For this demanding problem type, they propose an algorithm according to which first, Problem (5.16b) is solved for a parameter value which is assumed or taken from a previous iteration. Second, a nonlinear parameter estimation problem, subject to Equation (5.16a) is solved with local optimization, yielding an update for the parameters \( q \), and the loop is closed. Superficially, this approach may resemble [19], yet it is not quite the same since local solvers are used and \( X^{l,lp,E} \) is discrete.

In contrast to the present work, in our opinion, their method exhibits some limitations. First, it is not guaranteed to ensure the correct number of phases and/or phase splits as long as Problem (5.16b) is not solved to global optimality on a continuous set \( X^{l,lp} \) with appropriately specified bounds. On the other hand, convexity of \( \Delta G_{\text{ph}}(x_{\text{ph}}, \cdot) \) on \( X^{l,lp} = (0, 1)^{n_{x,lp}} \) would be too restrictive, as only \( \min \{ \Delta G_{\text{ph}}(x_{1}, \cdot), \Delta G_{\text{ph}}(x_{11}, \cdot) \} \) is required to be convex outside the phase split for a VLE. Second, there are additional constraints, cf. Figure 2.1d. Finally, the proposed algorithm in [47, 48] lacks a proof of convergence. In Section 5.4, a rigorous bilevel formulation is proposed to overcome these issues.

### 5.4 Proposed Bilevel Program

In order to avoid the violations of thermodynamic stability reported in Section 5.1, we extend the aforementioned works [148, 47, 107, 108, 20] to a parameter estimation problem for CEOS, subject to the necessary and sufficient criteria for thermodynamic stability. It may be interpreted either as an SIP [107] or as a BLP, according to the dependency of the objective on the constraints. As a third option, a trilevel problem formulation is briefly discussed in Appendix J.1. In the present work, we choose the BLP advocating that the
5.4 Proposed Bilevel Program

The objective is a function of the minimizers of, at least, some of the LLPs, while for others, the lower-level optimal objective function values only are of interest. In particular, we specify Problem (2.10) to the case of parameter estimation for CEOS in this chapter. The dedicated LLPs are presented in Sections 5.4.1 to 5.4.3 and serve the purpose of avoiding the issues in Figure 2.1.

The CEOS represents an equality constraint (EC) on the LLPs. It can be solved analytically; however, this would call for, e.g., if-else statements to handle the respective distinct analytical solutions, and thus, introduce nonsmoothness which has adverse effects on global optimization. Alternatively, the CEOS can be eliminated [112], yet only under certain conditions which are not guaranteed to be satisfied in this thesis. Therefore, in the present work, the CEOS is imposed as an EC on the lower level and its numerical solution is left to the sub-solvers.

What makes the formulation of a BLP and the LLPs embedded particularly difficult is the fact that the thermodynamic parameters \( q_u \) are variables during the regression and the number of real-valued solutions to the CEOS is, thus, not known a priori. Therefore, in this section, we present formulations of the LLPs accounting for this mathematical property of cubic equations by means of well-known mixed-integer formulations, a dependent variable which is piece-wise defined and/or the root discrimination criterion proposed in Section 5.2. It should be noted that in the following, \( v_{2,\text{llp}} \) denotes the root which is always undesired, \( v_{1,\text{llp}} \leq v_{2,\text{llp}} \leq v_{3,\text{llp}} \), and is excluded according to the well-known necessary criterion for mechanical stability. We close this section by giving the full BLP.

5.4.1 Lower-Level Problem: Baker’s Criterion

Baker’s criterion [12] consists of two parts: first, isopotential (5.13a) and (5.13b) and, second, the minimization of the tangent plane distance function to be captured by appropriate LLPs. See Appendix J.4.1 for a proof that the applicability of Baker’s tangent remains unaffected in the space of \((v_{1,\text{llp}}, x_{\text{llp}})\). For a violation of Baker’s criterion by an inadequate regression technique, see Figure 2.1a. In the following, we propose an LLP formulation that constrains the parameter estimation problem to those parameter values \( q_u \) such that the tangent be below the Gibbs free energy surface of the stable root for all mole fraction variables \( x_{\text{llp}} \). Therefore, let \( LLP_1 \) denote the respective set of these LLPs, \( D(\cdot) \) the discriminant of the cubic equation, \( f_{\text{ceos}, v}(\cdot) \) and \( f_{\text{ceos}, vv}(\cdot) \) the first and second derivative of the CEOS with respect to molar volume, respectively, \( \Delta \mu_{i,ph}(\cdot) \) the chemical potential, and \( ph \) the phase and \( r \) the type of root at some fixed point of tangency of Baker’s tangent. Then, the desired solutions to the CEOS in the LLP are captured by a set \( XV_{\text{LLP}_1} \), cf. [43, Definition 4], according to

\[
XV_{\text{LLP}_1} = \left\{ x_{\text{llp}}, v_{1,\text{llp}}, v_{3,\text{llp}} \mid \begin{align*}
&f_{\text{ceos}}(x_{\text{llp}}, v_{1,\text{llp}}, q_u) = 0, \\
&f_{\text{ceos}}(x_{\text{llp}}, v_{3,\text{llp}}, q_u) = 0, \\
&f_{\text{ceos}, v}(x_{\text{llp}}, v_{1,\text{llp}}, q_u) \geq 0, \\
&f_{\text{ceos}, vv}(x_{\text{llp}}, v_{3,\text{llp}}, q_u) \geq 0, \\
&D(x_{\text{llp}}, q_u) \cdot f_{\text{ceos}, vv}(x_{\text{llp}}, v_{1,\text{llp}}, q_u) \cdot f_{\text{ceos}, v}(x_{\text{llp}}, v_{3,\text{llp}}, q_u) \geq 0
\end{align*} \right\}
\]
In the following, Equations (5.17) and (5.18) are subsumed under $h^{EQ, llp}(\cdot) = 0$. So is our root discrimination criterion Equations (5.19) to (5.21) under $g^{EQ, llp}(\cdot) \geq 0$. With $x^{llp}, v^{llp}, v^{llp}_{3} \in XV_{LLP}$, we encode the well-known tangent plane distance function
\[
TPD\left(x^{llp}, v^{llp}_{1}, v^{llp}_{3}, x_{v}, v_{r}, q^{u}\right) = \min \left\{ \Delta G\left(x^{llp}, v^{llp}_{1}, q^{u}\right), \Delta G\left(x^{llp}, v^{llp}_{3}, q^{u}\right) \right\ } - \sum_{i} x^{llp}_{i} \Delta \mu_{i, ph}\left(x_{v}^{u}, v_{r}^{u}, q^{u}\right)
\]
by
\[
f^{llp}\left(x^{llp}, v^{llp}_{1}, v^{llp}_{3}, \phi^{llp}_{1}, x_{v}^{u}, v_{r}^{u}, q^{u}\right) = \phi^{llp}_{1} \Delta G\left(x^{llp}, v^{llp}_{1}, q^{u}\right) + \left(1 - \phi^{llp}_{1}\right) \Delta G\left(x^{llp}, v^{llp}_{3}, q^{u}\right) - \sum_{i} x^{llp}_{i} \Delta \mu_{i, ph}\left(x_{v}^{u}, v_{r}^{u}, q^{u}\right),
\]
\(\forall llp \in LLP_{1}\), where $\phi^{llp} \in \{0, 1\}$. By means of Equation (5.23) we then formulate a mixed-integer LLP according to
\[
\min \quad \text{s.t.} \quad f^{llp}\left(x^{llp}, v^{llp}_{1}, v^{llp}_{3}, \phi^{llp}_{1}, x_{v}^{u}, v_{r}^{u}, q^{u}\right) \quad (5.24a)
\]
\[
\begin{align*}
\text{h}^{EQ, llp}\left(x^{llp}, v^{llp}_{1}, v^{llp}_{3}, q^{u}\right) & = 0 \quad (5.24b) \\
\text{g}^{EQ, llp}\left(x^{llp}, v^{llp}_{1}, v^{llp}_{3}, q^{u}\right) & \geq 0, \quad (5.24c)
\end{align*}
\]
\(\forall llp \in LLP_{1}\). It should be noted that $x_{v}^{u}, v_{r}^{u}, q^{u}$ coming from the upper level are fixed. Problem (5.24) is feasible for any number of real-valued solutions to the CEOS. In the region of three real roots, the roots are discriminated, i.e., $v^{llp}_{1} \neq v^{llp}_{3}$, while in the single-real-root region, the roots coincide $v^{llp}_{1} = v^{llp}_{3}$.

Problem (5.24) works as follows: If $\exists v^{llp}_{1} \neq v^{llp}_{3}$ satisfying $h^{EQ, llp}(\cdot)$, then these are obtained by $g^{EQ, llp}(\cdot)$, and the lower-level objective function evaluated at the lower-level minimizer $f^{llp, \ast}(\cdot)$ is assigned the tangent plane distance function for the lowest Gibbs free energy branch by Equation (5.24a). On the other hand, if $\forall v^{llp}_{1} \neq v^{llp}_{3}$, then $v^{llp}_{1} = v^{llp}_{3}$ by $g^{EQ, llp}(\cdot)$, and the Gibbs free energy branches coincide. $f^{llp, \ast}(\cdot)$ is then correctly assigned the tangent plane distance function for this agnostic mixed-integer problem. As will be explained shortly, $f^{llp, \ast}(\cdot)$ is used to constrain the upper level of the BLP.

### 5.4.2 Lower-Level Problem: Mechanical Stability

As illustrated in Figure 2.1d, there is the need for constraining the regression to those $q^{u}$ that ensure the correct type of stable root $v^{llp}_{1}$ or else, there would be a risk to predict, e.g., roots that correspond to the vapor phase, while a liquid phase is observed in the experiments. This constraint is relevant only on a subset of $\{0, 1\}^{\mu^{llp}_{1}}$, namely outside the phase split. Therefore, let $g^{llp}_{1}(\cdot)$ denote a linear constraint to encode this fact, as well
as \( LL P_2 \) the respective set of these LLPs. As before, the desired solutions to the CEOS in these LLPs are captured by a set \( XV_{LL P_2} \equiv XV_{\{u\}} \). With \( x_{LLP}^1, v_{1,LLP}, x_{LLP}^3 \in XV_{\{u\}} \), we require a dependent variable \( y_{LLP}^1 \) which is piece-wise defined according to

\[
y_{LLP}^1 := \begin{cases} f_{LLP}^1 \left( x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3, x^u, q^u \right) \\ 0, \end{cases}
\]

with \( x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3 \in XV_{\{u\}}, \quad g_{LLP}^1 \left( x^u, x_{LLP}^1 \right) \geq 0 \) else, \( \forall LLP \in LL P_2 \). The lower-level objective function encodes the difference of the two Gibbs free energy branches in Figure 2.1 according to

\[
f_{LLP}^1 \left( x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3, x^u, q^u \right) = \Delta G \left( x_{LLP}^1, v_{1,LLP}^1, q^u \right) - \Delta G \left( x_{LLP}^1, v_{3,LLP}^3, q^u \right). \tag{5.26}
\]

In this case, we can even find a continuous LLP formulation by means of Equation (5.26) with the desired behavior of Equation (5.25). The formulation is given by

\[
\begin{align*}
\min_{x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3} & \quad f_{LLP}^1 \left( x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3, x^u, q^u \right) \\
\text{s.t.} & \quad g_{LLP}^1 \left( x^u, x_{LLP}^1 \right) \geq 0 \tag{5.27a} \\
& \quad h_{EQ, LLP}^1 \left( x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3, q^u \right) = 0 \tag{5.27b} \\
& \quad g_{EQ, LLP}^1 \left( x_{LLP}^1, v_{1,LLP}^1, v_{3,LLP}^3, q^u \right) \geq 0. \tag{5.27c}
\end{align*}
\]

\( \forall LLP \in LL P_2 \). Problem (5.27) is feasible for any number of real-valued solutions to the CEOS. \( g_{LLP}^1(\cdot) \) ensures that we consider mole fractions outside the phase split. If \( \exists v_{1,LLP} \neq v_{3,LLP} \) satisfying \( h_{EQ, LLP}^1(\cdot) \), then these are obtained by \( g_{EQ, LLP}^1(\cdot) \), and \( f_{LLP}^1(\cdot) \) is assigned the difference of Gibbs free energies according to Equation (5.26). On the other hand, if \( \# v_{1,LLP} \neq v_{3,LLP} \), then \( v_{1,LLP} = v_{3,LLP} \) by \( g_{EQ, LLP}^1(\cdot) \), and \( f_{LLP}^1(\cdot) = 0 \). As we will see shortly, the upper-level constraints are then trivially satisfied.

### 5.4.3 Lower-Level Problem: Convexity of the Stable Surface

As evident from Section 5.1 and Figure 2.1c, there is the need for constraining the regression to those \( q^u \) that ensure convexity of the lowest Gibbs free energy surface or else, there would be a risk to predict nonconvex surfaces at a mole fraction \( x_{LLP}^1 \) and hence, a risk of spurious phase splits. (See Appendix J.4.2 for a proof that the implications of local convexity of the Gibbs free energy in \( x_{LLP}^1 \) remain unaffected in the space \( \left( x_{LLP}^1, v_{1,LLP}^1 \right) \).) This constraint is relevant only on a subset of \( (0,1)^{u,\text{LLP}} \), namely outside the phase split. Therefore, as before, let \( g_{LLP}^1(\cdot) \) denote a linear constraint to encode this fact, as well as \( LL P_3 \) the respective set of these LLPs, \( ph \) the phase and \( r \) the type of root at some fixed point of tangency of Baker’s tangent. As illustrated in Figure 2.1c, \( v_{1,LLP}^1 \) and \( v_{1,LLP}^2 \) must be of the same type as the root at the adjacent predicted phase which is denoted by \( v_{1}^r \). This we encode by the root discrimination criterion in [83] considering the case of vanishing roots \( v_{r}^{1,LLP}, v_{r}^{2,LLP} \). Then, the desired solutions to the CEOS in the LLP are captured by a set \( XV_{\{u\}} \) according to

\[
XV_{\{u\}} = \left\{ x_{LLP}^1, x_{LLP}^2, v_{1,LLP}^1, v_{1,LLP}^2, v_{1}^r, v_{2}^r \right\}
\]
Parameter Estimation of Cubic Equations of State (CEOS)

\[ f_{\text{ceos}}(x^{l,1,llp}, v_r^{l,1,llp}, q^u) = 0, \]  
(5.28) 
\[ f_{\text{ceos}}(x^{l,2,llp}, v_r^{l,2,llp}, q^u) = 0, \]  
(5.29) 
\[ f_{\text{ceos},v}(x^{l,1,llp}, v_r^{l,1,llp}, q^u) \geq 0, \]  
(5.30) 
\[ f_{\text{ceos},v}(x^{l,2,llp}, v_r^{l,2,llp}, q^u) \geq 0, \]  
(5.31) 
\[ \text{sign}(f_{\text{ceos},v}(x^v, v_r^u, q^u)) = \text{sign}(f_{\text{ceos},v}(x^{l,1,llp}, v_r^{l,1,llp}, q^u)), \]  
(5.32) 
\[ \text{sign}(f_{\text{ceos},v}(x^v, v_r^u, q^u)) = \text{sign}(f_{\text{ceos},v}(x^{l,2,llp}, v_r^{l,2,llp}, q^u)). \]  
(5.33)

In order to cast Equations (5.28) to (5.33) as mixed-integer constraints suitable for the LLPs, we follow [83] and use a big-M formulation, where \( \theta_u, \theta_{2,llp}, \theta_{3,llp} \in \{0, 1\} \) denote some binary variables, and \( M_u, M_{2,llp}, M_{3,llp} \in \mathbb{R}_{>0} \) constants whose values are sufficiently large to relax the following constraints. Then, Equations (5.32) to (5.33) can be reformulated to

\[ f_{\text{ceos},v,v}(x^u, v_r^u, q^u) \geq -\theta_u \cdot M_u \]  
(5.34) 
\[ -f_{\text{ceos},v,v}(x^u, v_r^u, q^u) \geq -(1 - \theta_u) \cdot M_u \]  
(5.35) 
\[ f_{\text{ceos},v,v}(x^{l,1,llp}, v_r^{l,1,llp}, q^u) \geq -\theta_{2,llp} \cdot M_{2,llp} \]  
(5.36) 
\[ -f_{\text{ceos},v,v}(x^{l,1,llp}, v_r^{l,1,llp}, q^u) \geq -(1 - \theta_{2,llp}) \cdot M_{2,llp} \]  
(5.37) 
\[ f_{\text{ceos},v,v}(x^{l,2,llp}, v_r^{l,2,llp}, q^u) \geq -\theta_{3,llp} \cdot M_{3,llp} \]  
(5.38) 
\[ -f_{\text{ceos},v,v}(x^{l,2,llp}, v_r^{l,2,llp}, q^u) \geq -(1 - \theta_{3,llp}) \cdot M_{3,llp}. \]  
(5.39)

In the following, Equations (5.28) and (5.29) are subsumed under \( h^{EQ,llp}(-) = 0 \), and Equations (5.30), (5.31), (5.34) to (5.39) under \( g^{EQ,llp}(-) \geq 0 \). With \( x^{l,1,llp}, x^{l,2,llp}, v_r^{l,1,llp}, v_r^{l,2,llp} \in \mathbb{X}_{V,LLP_3} \), again, we propose a substitution of the lower-level objective function by a dependent variable \( y^{llp} \) which is piece-wise defined according to

\[ y^{llp} := \begin{cases} 
    f^{llp}(x^{l,1,llp}, x^{l,2,llp}, v_r^{l,1,llp}, v_r^{l,2,llp}, q^u) \\
    \text{with } x^{l,1,llp}, x^{l,2,llp}, v_r^{l,1,llp}, v_r^{l,2,llp} \in \mathbb{X}_{V,LLP_3}, \\
    g^{l,1,llp}(x^u, x^{l,llp}) \geq 0 \\
    \wedge (2\theta_u - \theta_{2,llp} - \theta_{3,llp}) = 0 \\
    0, \\
    \text{else,} 
\end{cases} \]  
(5.40)

\forall llp \in LLP_3. The lower-level objective function encodes the well-known tangent plane distance function for a moving point of tangency in Figure 2.1c according to

\[ f^{llp}(x^{l,1,llp}, x^{l,2,llp}, v_r^{l,1,llp}, v_r^{l,2,llp}, q^u) = \Delta G(x^{l,2,llp}, v_r^{l,2,llp}, q^u) - \sum_i^l \Delta \mu_{i,ph}(x^{l,1,llp}, v_r^{l,1,llp}, q^u). \]  
(5.41)

By means of Equation (5.40) we finally, propose a mixed-integer LLP which reads

\[ \min y^{llp} \]  
(5.42a)

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This approach introduces some inaccuracy. For instance, see shortly, the upper-level constraints are then trivially satisfied. It should be noted that side (RHS) holds. The same applies to mole fractions within the phase split. As we will see of a tangent with a moving point of tangency, on the upper level. On the other hand, if both \( v_r^{1,\text{llp}} \) and \( v_r^{2,\text{llp}} \) satisfying \( h^{\text{EQ,\text{llp}}} (\cdot) \) and of the same type as \( v_r^u \), then \( 2\theta_u - \theta_2^{\text{llp}} - \theta_3^{\text{llp}} = 0 \).

As a result, Equation (5.41) imposes convexity of the Gibbs free energy surface, in the form of a tangent with a moving point of tangency, on the upper level. On the other hand, if \( v_r^{1,\text{llp}} \) or \( v_r^{2,\text{llp}} \) are not of the same type as \( v_r^u \), then \( 2\theta_u - \theta_2^{\text{llp}} - \theta_3^{\text{llp}} \neq 0 \), and the right-hand side (RHS) holds. The same applies to mole fractions within the phase split. As we will see shortly, the upper-level constraints are then trivially satisfied. It should be noted that this approach introduces some inaccuracy. For instance, \( v_r^u \) and \( v_r^{1,\text{llp}} \) are considered to be of the same type, even if, e.g., \( f_{\text{ceos,vv}} (x^u, v_r^u, q^u) > 0 \), yet \( f_{\text{ceos,vv}} (x^{1,\text{llp}}, v_r^{1,\text{llp}}, q^u) = 0 \) which is deemed acceptable.

5.4.4 Lower-Level Problem: Correct Number of Phases

From Figure 2.1b it follows that the regression needs to be restricted to those \( q^u \) that avoid spurious points of tangency or else, there would be a risk to predict spurious phases, also see Section 4.1.2. The approach is very close the one in Section 5.4.1 with the exception of enforcing the LLP only on a subset of \((0, 1)^{n_{\text{llp}}^u} \), namely within the phase split. Additionally, \( TPD(\cdot) > 0 \) becomes a strict inequality, in order to avoid not only intersections but even points of tangency. For global optimization, this can be reformulated to a closed inequality by introducing some small tolerance.

5.4.5 Problem Statement

In this section, we specify Problem (2.10) to the case of parameter estimation for CEOS. A general structure of the program is given by Problem (5.43), also see [43, (BLP)].

\[
\min_{x^u, v_1^u, v_3^u, q^u} f^u(x^u, v_1^u, v_3^u, q^u) \tag{5.43a}
\]
\[
s.t. h^u (x^u, v_1^u, v_3^u, q^u) = 0 \tag{5.43b}
\]
\[
g^u (x^u, v_1^u, v_3^u, q^u) \geq 0 \tag{5.43c}
\]
\[
f^{1,\text{llp},u} (x^u, q^u, v_r^u) \geq 0, \forall llp \in LLP_1 \tag{5.43d}
\]
\[
f^{1,\text{llp},u} (x^u, q^u) \geq 0, \forall llp \in LLP_2 \tag{5.43e}
\]
\[
y^{1,\text{llp}} (x^u, q^u, v_r^u) \geq 0, \forall llp \in LLP_3 \tag{5.43f}
\]
\[
\begin{pmatrix}
x^{u,\text{llp}}
v_1^{u,\text{llp}}
v_3^{u,\text{llp}}
\end{pmatrix} \in \text{argmin} \text{ Problem (5.24), } \forall llp \in LLP_1
\]
Parameter Estimation of Cubic Equations of State (CEOS)

\[
\begin{bmatrix}
x_1^{u,lp} \\
v_1^{u,lp} \\
v_3^{u,lp}
\end{bmatrix} \in \arg\min_{x_1^{l,lp}, v_1^{l,lp}, v_3^{l,lp}} \text{Problem (5.27), } \forall llp \in LLP_2
\]

\[
\begin{bmatrix}
x_1^{u,lp} \\
x_2^{u,lp} \\
v_1^{u,lp} \\
v_2^{u,lp}
\end{bmatrix} \in \arg\min_{x_1^{l,lp}, x_2^{l,lp}, v_1^{l,lp}, v_2^{l,lp}} \text{Problem (5.42), } \forall llp \in LLP_3
\]

\[
x^{llp} \in X^{l,lp}, v^{llp} \in V^{l,lp}, x^{u,lp} \in X^{u,lp},
\]

\[
v^{u,lp} \in V^{u,lp}, x \in X^u, v^u \in V^u, q^u \in Q^u,
\]

where \(v_r\) takes \(r \in \{1, 3\}\) as required for mechanical stability. This is an extension of Problem (2.10) in the sense that \(v_r\) is an additional variable; it is required to capture the mechanical equilibrium in addition to the phase equilibrium.

For the sake of brevity, we omit the auxiliary integer variables, as well as variables \(x^{u,lp}, v_1^{u,lp}, v_3^{u,lp}\) \(\forall llp\) in Equation (J.1a). It may represent, e.g., a least-square error to indicate the goodness of fit, while Equation (5.43b) imposes isopotential (cf. Equations (5.13a) and (5.13b)), and Equation (5.43c) discriminates the roots to the CEOS.

The LLPs presented in Sections 5.4.1 to 5.4.3 either communicate the lower-level objective function evaluated at the lower-level minimizer \(f^{l,lp,*}(\cdot)\) or a dependent variable \(y^{l,lp}\) to the upper level. Both are parametric in the upper-level variables. \(y^{l,lp}\) ensures that Equation (5.43f) can be evaluated, even if the lower-level objective function \(f^{l,lp}(\cdot)\) is not valid. For instance, in Section 5.4.3, this is the case if the desired roots to the CEOS do not exist. Then, the LLPs switch to \(y^{l,lp} = 0\), and Equation (5.43f) is trivially satisfied. This is justified, as from a thermodynamic point of view, the situation denoted by \(iii\) cannot violate thermodynamic stability. If, however, the desired roots do exist, then \(y^{l,lp}\) is set to \(f^{l,lp,*}(\cdot)\).

\(f^{l,lp}(\cdot)\) encodes differences of Gibbs free energy terms, e.g., the well-known tangent plane distance function [12] and thus, additional constraints (5.43d) to (5.43f) impose that these differences be positive. (This has the effect of some notational differences only between this work and [43] in the approximation of the optimal lower-level objective function by a discretization of the lower-level variables.) Consequently, for the optimal thermodynamic parameter \(q^{u,*}\), there exists a bilevel-feasible solution that satisfies Equations (5.43b) to (5.43f) and global optimality of the LLPs. As opposed to the formulations from the literature, cf. Section 5.3.1, only in Problem (5.43), those criteria are considered that are both sufficient and necessary for thermodynamic stability.

5.4.6 Constraint Qualifications

From Equations (5.17) and (5.18), it can be inferred that LICQ is violated in some of the LLPs if there exists a single real root. Following the argumentation in Section 5.2.2, this should not be problematic for the proposed method.
5.5 Case Studies

The proposed formulation is tested on two case studies, the standard fluid system C$_5$H$_{12}$/H$_2$S with PR and SRK. Due to the fact that even the sub-problems of Problem (5.43) are computationally challenging, unfortunately, to date, the proposed method cannot be applied to the case studies in Section 5.1. In particular, the global solver BARON [161] reports infeasibility of the LBP upon time-out. This can be attributed to both the presence of challenging nonconvex terms in the CEOS models [72] and a bad scaling spanning eight orders of magnitude; however, there is no obvious way to rescale. One potential approach to achieve better results with BARON seems to be the use of the root discrimination criterion in [83], if applicable, in particular when the desired roots exist. Since this is satisfied for the present case studies, we use [83] in the implementation. Altogether, as BOARPET relies on BARON as a sub-solver, our work is currently limited to these two case studies as a first step towards full industrial problems.

5.5.1 Computational Details

Optimization Algorithm

Problem (5.43) is a BLP with CEOS as equality constraints in the LLPs. Hence, the program is solved with the algorithm in [43] which extends [110] to ECs on the lower level. According to the algorithm a relaxation of Problem (5.43), a so-called lower-bounding problem (LBP) is solved followed by all of the LLPs. If the LLPs satisfy $y^{l,illp} \geq 0$, $\forall llp \in LLP$, thermodynamic stability is guaranteed and the algorithm terminates, else the LBP is tightened. In particular, logical constraints are imposed that approximate the optimal objective functions of the LLPs, making the LBP a Mixed-Integer Nonlinear Program (MINLP). Under similar assumptions as in [110] and an additional uniqueness assumption on the solution of the ECs, the algorithm is guaranteed to terminate finitely [43, Assumption 4].

For the present problem, the mole fractions are independent variables on the lower levels, while the molar volumes are dependent variables that are uniquely defined by the CEOS and an appropriate root discrimination criterion denoted by $g^{EQ,illp}(\cdot)$. From thermodynamics, a well-known criterion is given by

$$v^{l,illp} \in \arg \min \left\{ \Delta G(x^{l,illp}, v_1^{l,illp}, q^n), \Delta G(x^{l,illp}, v_2^{l,illp}, q^n), \Delta G(x^{l,illp}, v_3^{l,illp}, q^n) \right\}, \quad (5.44a)$$

$$\iff v^{l,illp} \in \arg \min \Delta G(x^{l,illp}, v_1^{l,illp}, q^n), \text{ s.t. } f_{cos} \left( x^{l,illp}, v_1^{l,illp}, q^n \right), \quad (5.44b)$$

where $v^{l,illp} (x^{l,illp}, q^n)$ is the desired solution to the CEOS, which is parametric in two variables. There are considerable advantages of the discrimination according to Equation (5.44). First, the program is feasible by the fundamental theorem of algebra for a cubic equation, i.e., the existence of the parametric solution is guaranteed. Second, the solution is unique since it is the global minimizer (multiplicity of the global minimizer is not problematic). Third, due to the physical nature of the CEOS, the solution is continuous in $q^n$ on $Q^u$ and in $x^{l,illp}$ on $X^{l,illp}$. In particular, if $\Delta G(x^{l,illp}, v^{l,illp}, q^n)$ is continuous in these variables, then [43, Assumption 4] on uniqueness, continuity and existence of the parametric solution is satisfied. From numerical studies, to date, we have not observed any cases...
in which it is violated. Therefore, at least, for the present case studies, the algorithm is
applicable to Problem (5.43). It should be noted that a violation of the continuity and/or
uniqueness assumption does not necessarily disable convergence in practice. In order to
solve the case studies, we replace Equation (5.44) by certain ICs denoted by \( g^{EQ,lp}(\cdot) \)
and implement those parts from [43] required for our problem type. We, thus, extend our
in-house regression tool BOARPET.

Commercial Sub-Solvers

The in-house regression tool BOARPET implements Problem (5.43). It relies on commer-
cial sub-solvers through GAMS 24.9.2. We use a 64-bit xenon processor 2.60 GHz running
Windows 2008 R2 data center. For the LBP, KNITRO [28] and BARON [161] are called
in a row with the following settings, for KNITRO: \textit{algorithm} 4, and for BARON: \textit{AbsCon-
FeasTol} 1e-7, \textit{RelConFeasTol} 0, \textit{NlpSol} -1, \textit{LpSol} 3, \textit{BoxTol} 1e-5, \textit{FirstFeas} 0, \textit{NumSol}
100, \textit{NumLoc} 1, \textit{reslim} 120s, and the thermodynamic parameter is prioritized over mole
fractions. KNITRO is used to identify a feasible or locally optimal point, in order to ini-
tialize BARON. BARON settings for the LLPs are: \textit{AbsConFeasTol} 1e-7, \textit{RelConFeasTol}
0, \textit{BoxTol} 1e-5, \textit{Lpsol} 3, \textit{Nlpsol} -1, \textit{NumLoc} 10. Both the LBP and the LLPs
represent demanding NLPs. In particular, the cubic equality and reformulations result in
slow convergence if at all, within 1200s. However, a solution time of, at most, a couple of
minutes per LLP is deemed acceptable. Alternatively, applying ANTIGONE [104] results
in faster convergence in some cases, but also in failures in others and thus, ANTIGONE
is no longer considered.

Models

For a binary fluid system, the upper-level objective function (5.43a) reads
\[ f^u = \sum_{ph=1}^{P} \left( x_{i,ph,\text{meas}} - x_{i,ph}^u \right)^2. \]
Instead of the molar volume we choose the compressibility factor \( Z_r \) as variable for the CEOS due to its improved scaling and allowing for a better approx-
imation of box constraints; the variables are subject to the following box constraints
\[ x_{l,lp}^{u} \in [\epsilon_{r}, 1 - \epsilon] n_{r,lp}^{u}, x_{u,lp}^{u} \in [\epsilon_{r}, 1 - \epsilon] n_{r,lp}^{u}, v_{r}^{u} \in [\epsilon_{r}, 1 - \epsilon] n_{r,lp}^{v}, q_{u}^{u} = k_{n,ij}, \]
where \( k_{n,ij} \in [-1, 1] \) denotes the regressed binary interaction parameter and is initialized with zero. SRK [156] and PR [127] with
dW mixing and combining rules are applied, cf. the Appendix J.2. \( T, P \) are held const.
At each measurement datum, several LLPs are imposed in Problem (5.43), giving 56 LLPs
in total for each of the \( C_5H_{12}/H_2S \) case studies. In order to keep computational times
tractable, we discretize the LLPs in the mole fraction space by means of a grid of 30
equidistant supporting points per mole fraction variable, i.e., \( x_{i,lp}^{u} \in \{x_{i,1}^{lp}, \ldots, x_{i,30}^{lp}\} \), to
each of which a (continuous) compressibility factor variable corresponds. As a result, the
convergence of BARON is significantly improved, however, at the expense of the guaran-
tee of global optimality. The number of sub-problems thus introduced scales linearly or
quadratically in the number of supporting points, depending on the LLP. CPU times are
around 4.5h per case study.
5.5 Case Studies

R gibbs

For the flash calculations in Section 5.1, we use Aspen Plus [7] on a 64-bit xenon processor 2.60 GHz running Windows 2008 R2 data center, and the following settings for RGibbs: for CF$_4$/CHF$_3$ “Include vapor phase” false, “Calculate phase equilibrium only”, “Maximum number of fluid phases” 2, “Maximum number of iterations” 500 to allow convergence, for acetone/water “Include vapor phase” false, “Calculate phase equilibrium only”, “Maximum number of fluid phases” 2, for methanol/benzene “Include vapor phase” true, “Calculate phase equilibrium only”, “Maximum number of fluid phases” 3. The feed streams and RGibbs operate at the same temperature and pressure as given in the captions of the respective figures. Only for methanol/benzene, we use a feed at a slightly higher temperature (302.0 K). For the results in Appendix J.3, we use RGibbs with the settings: “Include vapor phase” true, “Calculate phase equilibrium only”, “Maximum number of fluid phases” 3, and the feeds 0.05, 0.1, 0.2, 0.3, 0.4, 0.6 and 0.8, respectively.

5.5.2 C$_5$H$_{12}$/H$_2$S

Despite of the VLE of C$_5$H$_{12}$/H$_2$S commonly occurring in natural gas reservoirs, there is no $k_{a,ij}$ available in the data bank of Aspen DRS [8] for the SRK model. In this section, both PR and SRK are fitted to a selection of measurement data from [140] as given in Appendix J.3.

The LBP is initialized with empty discretization sets in the first iteration of the bilevel algorithm, so that in principle, Problem (5.13) is solved, followed by all of the LLPs in Problem (5.43). The bilevel algorithm converges and thus, thermodynamic stability is satisfied and the erroneous behavior in Figure 2.1 is avoided for the solution. Since the sets are empty upon convergence, one might easily conclude that Problem (5.13) was sufficient for these two case studies. It should be noted, however, that thermodynamic stability within the accuracy of the applied discretization scheme is not guaranteed by Problem (5.13) only.

Figure 5.6 depicts the Gibbs free energy branches resulting each from a different root to the CEOS, along with the supporting tangent. As shown in the figures, Baker’s criterion, the correct number of phases, as well as the correct number of phase splits is satisfied. Further, in Figure 5.6, there are domains $X^{Llp}$ on which only one of the two required solutions $v^{Llp}_l$ exists calling for the formulations in Section 5.4.

The methods in [126] and those implemented in Aspen do not give the aforementioned guarantees. For the sake of completeness, we perform a posteriori checks similar to Figure 5.6, and find that the criteria are satisfied and that the regressed parameters from [126] and Aspen are indeed applicable. This is not necessarily the case for standard regression formulations as demonstrated in Section 5.1.

The predicted mole fractions and compressibility factors for both phases are given in Appendix J.3 for the two models, along with the flash results of RGibbs. The compressibility factors take reasonable values and allow a clear distinction of vapor from liquid which indicates that the method reliably considers mechanical stability. The flash results match the predicted mole fractions within a tolerance of less than 2.5 %, and the regressed parameters are, thus, applicable in the process simulation in contrast to the parameters discussed in Section 5.1. As depicted in Figure 5.7 and the value of $f_{u,*}$ in Tables 5.6 and 5.7 the fit is acceptable, considering that $P = const.$ during the regression and only one parameter per
Fig. 5.6: Gibbs free energy $\Delta G$ with respect to mole fraction of pentane, for VLE of C$_5$H$_{12}$/H$_2$S, $k_{a,ij} = 0.0645$ (PR) from this work. Left: at 344.23 K, 2757.9 kN m$^{-2}$, right: at 344.23 K, 689 kN m$^{-2}$. Red dashed line: Baker’s tangent, blue solid curve: liquid, green dashed curve: vapor, red cross: predicted mole fraction.

Fig. 5.7: Pressure $P$ over mole fraction of pentane at 344.23 K, for VLE of C$_5$H$_{12}$/H$_2$S, $k_{a,ij} = 0.0645$ (PR), $k_{a,ij} = 0.0713$ (SRK) from this work. The curves practically coincide.

Table 5.6: Regression results with BOARPET [109] for $k_{a,ij}$ of VLE of C$_5$H$_{12}$/H$_2$S in comparison to results from the literature. The PR model is fitted to isothermal VLE data from [140] as given in Appendix J.3.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$k_{a,ij}$</th>
<th>$J^{\text{**}}$</th>
<th>Validity</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>0.064493</td>
<td>0.00643</td>
<td>689.48 - 4826.33 kN m$^{-2}$</td>
<td>[140]</td>
</tr>
<tr>
<td>[8]</td>
<td>0.063</td>
<td>not given</td>
<td>not given</td>
<td>not given</td>
</tr>
<tr>
<td>[126]</td>
<td>0.0633</td>
<td>not given</td>
<td>not given</td>
<td>[140]</td>
</tr>
</tbody>
</table>
5.6 Interim Conclusions

In this chapter, we demonstrate that the regression of CEOS models using standard formulations can entail erroneous process simulation results in Aspen Plus, in particular a violation of thermodynamic stability. As opposed to conventional programs, a BLP allows the parameter regression for CEOS models, subject to the necessary and sufficient criteria for the satisfaction of thermodynamic stability. As a special feature of the formulation proposed in this chapter, the regression results are guaranteed to satisfy Baker’s criterion in the variable space of mole fractions. The satisfaction of the mechanical stability, on the other hand, is ensured by a dedicated root discrimination criterion, among others. A proof-of-concept of the new method is given by the VLE of C\textsubscript{5}H\textsubscript{12}/H\textsubscript{2}S with SRK and PR, for which the BLP is solved by means of global deterministic optimization. Since the sub-problems are numerically challenging for state-of-the-art global solvers, most of them are solved in a discretized variable space. The regressed binary interaction parameters could complement the data base of Aspen DRS. In the mathematical context of Chapter 2, we conclude that only the BLP will yield a solution (x\textsuperscript{u,*}, q\textsuperscript{u,*}) of Problem (5.43) which provides the desirable guarantee that a reliable (P,T)-flash correctly regain x\textsuperscript{u,*} upon use of q\textsuperscript{u,*}.

Unfortunately, to date, industrial case studies do not seem computationally tractable for our method as long as it relies on general-purpose commercial solvers. As such, the present work motivates the need for dedicated global solvers that exploit the convex underestimators and concave overestimators of CEOS models of, e.g., [72], and that exhibit robust

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**Table 5.7:** Regression results with BOARPET [109] for k\textsubscript{a,ij} of VLE of C\textsubscript{5}H\textsubscript{12}/H\textsubscript{2}S in comparison to results from the literature. The SRK model is fitted to isothermal VLE data from [140] as given in Appendix J.3. Aspen DRS [8] does not provide a value.

<table>
<thead>
<tr>
<th>Reference</th>
<th>k\textsubscript{a,ij}</th>
<th>f\textsuperscript{a,*}</th>
<th>Validity</th>
<th>Measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>0.071294</td>
<td>0.00633</td>
<td>689.48 - 4826.33 kN m\textsuperscript{-2}</td>
<td>[140]</td>
</tr>
<tr>
<td>[8]</td>
<td>not given</td>
<td>not given</td>
<td>not given</td>
<td>not given</td>
</tr>
<tr>
<td>[126]</td>
<td>0.070</td>
<td>not given</td>
<td>not given</td>
<td>[140]</td>
</tr>
</tbody>
</table>

CEOS model is regressed. However, we cannot claim that the fit is optimal, as BARON does not converge in 1200 s (LBD of the LBP is 0). The fit obtained with the literature parameter values (not shown here for brevity) is similar to the one obtained in this section. In addition, Figure 5.7 shows that PR and SRK perform equally well. Finally, in Tables 5.6 and 5.7, the resulting values of k\textsubscript{a,ij} are given. These are close for both models, and in good agreement with the results from the literature. It should be emphasized that for the latter, however, there is no guarantee of thermodynamic stability by the methods themselves but only by our a posteriori checks. Generally speaking, these a posteriori checks can be more efficient than solving the BLP as long as they only confirm thermodynamic stability. Should the a posteriori checks, however, reveal a violation of thermodynamic stability, there would at best, be heuristics on how to correct the parameter values. In contrast, the BLP follows a systematic procedure that is guaranteed to converge to the correct parameter values [43] and can thus, turn out to eventually, be even more efficient than a posteriori checks.
rescale functionalities. As future steps, the method may be extended to noncubic equations of state, such as PC-SAFT, provided an appropriate root discrimination criterion is amenable.
6 Conclusions and Future Work

In the following, the interim conclusions given in each chapter are summarized, and an outlook on future work is given.

6.1 Conclusions and Potential Impact

Disclaimer: This section adopts some sentences from the section entitled “Introduction” in [63] and from the abstract in [62].

As an overarching theme, this thesis gives evidence that phase equilibrium thermodynamics is an application of global optimization in which it can be particularly problematic to rely on local methods only. The reason for this is that thermodynamic stability can only be decoded by a global optimization problem. Therefore, as main contributions, this thesis i) assesses the problem formulations that established phase equilibrium regression tools implement, in particular the guarantees they provide of the satisfaction of thermodynamic stability, ii) highlights how violation of thermodynamic stability can affect the process simulation/optimization, and finally, iii) proposes formulations covering the mechanical equilibrium, the phase equilibrium, and the chemical reaction equilibrium, in order to overcome these issues and to provide reliable regression results.

This thesis includes some mathematical proofs using (elementary) linear algebra, the calculus of cubic functions, and KKT theory or related applications such as complementary slackness conditions, mixed-integer problems and constraint qualifications. From among thermodynamic methods, the (reactive) tangent plane criteria and thermodynamic stability for the mechanical equilibrium, the phase equilibrium, and the chemical reaction equilibrium are used. In the following, the author’s contributions to developing new methodologies by means of these fundamentals, as well as to providing practical examples are given chapter-wise.

Chapter 2 provides the mathematical preliminaries taken from the literature. As a contribution of the author, a generic BLP interpretation of the GSIP in [108, 107, 20] is proposed, and further specified in the following chapters. [31, 148, 54, 53] are probably closest to this work. However, these do not cover all aspects of violation of thermodynamic stability and/or provide no systematic feedback in case of its violation which is done in this thesis. Further, KKT theory is used to show that standard tools implementing standard formulations can be unreliable, e.g., if these substitute even nonconvex LLPs by their KKT conditions. The author advocates the importance of the bilevel method since it is the nonconvex LLPs that are prevalent for industrial regression. In particular, we prove conditional convexity of a Gibbs model [61] recently proposed in [144].

In Chapter 3, the implementation of the BLP, the regression tool BOARPET (Bilevel Optimization Algorithm for Rigorous and Robust Parameter Estimation in Thermodynamics) is presented, and the author’s contributions to making the original code of Mitsos a computational tool used for industry through DEHEMA DPP (Data Preparation Package)
are given. Further, the theoretical assessments of the previous chapter are supported by
umerical proofs in the form of qualitative solver comparisons of BOARPET to Aspen DRS
(Data Regression System), as well as to GN (Gauss-Newton) through DPP, for parameter
estimation of activity coefficient models in nonreactive systems. It is found that BOAR-
PET reliably reports only bilevel-feasible points whereas, in some cases, the standard tools
unexpectedly even lead to a violation of the KKT second-order sufficient conditions [59]
and/or thermodynamic constraints of which discretization-based implementations are well
known. It should be noted that straightforward improvements for DRS were communi-
cated to the developers upon request. To the users, on the other hand, we give ready-to-use
advice on how to check the regression results of commercial tools within those very tools,
since said violations, unfortunately, are not reported by the tools [59].

As a further outcome of Chapter 3, reliable parameter values of the LLEs of 2MTHF/H\textsubscript{2}O
[59] and 3MTHF/H\textsubscript{2}O [88] are available to, e.g., modeling extraction columns in future
biorefineries. For the first use case, the regressed parameter values capture a particularly
broad temperature range compared to the open literature, whereas for the second, the au-
thor’s contribution is the first to report parameter values and a valid model. Furthermore,
in a first assessment, MF-derivatives are found to be more advantageous solvent and ready-
to-use biofuels than THF-derivatives. These results are based on simple purity criteria and
a small selection of these compounds, and require further, more detailed considerations.
Chapter 4 extends [108, 107, 20] to both phase and chemical reaction equilibrium, that
is, data regression of equilibrium-limited reactions. To the author’s best knowledge, the
methodology proposed in [63] is unprecedented in the open literature which, to date, mainly
relies on the equilibrium constant method. By an illustrative case study it is numerically
proven that in certain cases, the equilibrium constant method fails, while the BLP returns
reliable parameter values. It is discussed how the erroneous results of the equilibrium con-
stant method can lead to costly and inappropriate process design decisions. As a further
contribution in Chapter 4, an SIP reformulation of the GSIP in [108, 107, 20] is presented
based on the literature, making the solution of the regression problem amenable to a wider
class of optimization algorithms.

Chapter 5 extends [108, 107, 20, 148, 47] to both phase and mechanical equilibrium for
the regression of CEOS models. The methodology proposed in [60] has not been reported
in the open literature which, to date, mainly relies on the isopotential method and, at
best, on the necessary criteria for the mechanical equilibrium. As a first major outcome, a
continuous volume-root discrimination criterion is presented which exploits the well-known
method of Cardano and can handle situations in which the cardinality of the solution set is
not known a priori [62]. Second, it is illustrated how erroneous regression results reported
by standard methods can affect the process simulation in practice, using RGibbs [7]. As
a first step towards industrial case studies, the ability of the proposed BLP to overcome
this deficiency is demonstrated by means of a proof-of-concept.

The methods in Chapters 4 and 5 have not reached the same degree of maturity, yet,
as the methods in Chapter 3 which would, however, be required for the full industrial
use. For instance, the root discrimination formulation and the parameter estimation for
CEOS are implemented in BOARPET, whereas the implementation for reactive mixtures
consists of hard-coded GAMS problems called via a script. It should be emphasized that
the methods in this thesis are, thus, not amenable to industrial practice, yet. One of the
reasons for this is that these rely on global deterministic optimization and thus, can be
computationally challenging. In most cases, the author had to resort to small-size prob-
lems to serve as proofs-of-concept of her methods, due to the computational limits of the state-of-the-art global solvers, such as BARON [161] and ANTIGONE [104]. These issues were discussed with the respective developers and to the author’s best belief, potentially helped to improve the solver codes. In some cases, however, the issues could not be resolved. For instance, the problems in Chapter 5 are reportedly not sufficiently well scaled for BARON. In particular, it reports the trivial solution instead of the expected VLE, and does not converge in reasonable time ($\approx 10$ h). In terms of ANTIGONE, some issues with constraint violations arose, so that it was no longer used in this thesis.

### 6.2 Future Work

From the interim conclusions in Chapters 3 to 5, certain subjects of potential future research arise which will be outlined in the following. For instance, with rather low effort, the formulation in Problem (2.10) can be extended to multi-component mixtures of $N$ species. However, this would require major changes in the implementation BOARPET [109]. This is due to the fact that the number of constraints in Problem (2.10) scales linearly in $N$, and the number of variables linearly to quadratically in $N - 1$, depending on the particular type of LLP. As a result, the implementation of the LLPs can become involved, considerably increasing computational time, if not even hitting the limits of the state-of-the-art global sub-solvers BOARPET relies on. For instance, for those LLPs for which $llp \in LLP_3$, an $(N - 1) \times (N - 1)$ Hessian $H$ needs to be checked for positive definiteness. In order to reduce computational effort, checks for the necessary conditions only could be performed a priori, e.g., on $\det H > 0$. On the other hand, for $llp \in LLP_2$ and those that prevent spurious phases, it follows from Gibb’s phase rule [116, 50, 105, 139] that the number of phases and thus, the number of said LLPs scales linearly in $N - 1$. In these cases, a necessary criterion cannot be used, in order to prematurely confirm the violation of thermodynamic stability and to save computational resources. The reason for this is that the bilevel algorithm [110] is guaranteed to converge in finite time only if the discretization sets are populated completely, that is, if all of the LLPs are solved to global optimality. As a specific idea for the implementation of the discretization of the lower-level variable space in the LBP, the author recommends to discretize all of the $N - 1$ lower-level mole fraction variables on $[0, 1]$, and to enforce the closure condition using GAMS built-in conditionals.

Addressing the issue of automated process design, the effects of functional groups, such as double bonds, cyclic structures, methyl- and ether-groups could be explored using machine learning algorithms. For instance, a neural network could be trained on the data base of platform, solvent, intermediate and biofuel candidates within TMFB. Thus, certain rules would be identified as a link between these functional groups and, e.g., the width of respective miscibility gaps. In a next step, these rules could be used in the context of product design to predict suitable biofuel candidates that allow a low separation effort.

As mentioned before, in Chapters 4 and 5, we observe that state-of-the-art general-purpose global solvers, unfortunately, hit their limits when given the sub-problems derived from Problem (2.10). On the other hand, there exist numerous dedicated global solvers relying on, e.g., interval analysis [77, 78, 176] or branch-and-bound algorithms for thermodynamic flash problems [97, 99, 98, 100, 72], as well as for (single-level) parameter
estimation problems [54, 53, 55, 152]. As these represent a considerable portion of the sub-problems of Problem (2.10), namely \( llp \in LLP_2 \) and a (simplified) LBP, respectively, an extension of these dedicated methods to all of the sub-problems is conceivable. The convex under-estimators and concave over-estimators of thermodynamic models based on, e.g., interval extensions and \( \alpha - BB \) relaxations proposed in, e.g., [72], also see Table 2.3.2, or McCormick relaxations are of particular interest. For instance, \( x \ln(x) \) is a prominent term in thermodynamics, and only recently has been added to the library of convex functions of the general-purpose solver BARON [161], while the dedicated solver in [98] has been exploiting the mathematical properties of \( x \ln(x) \) for years. Besides convexity and concavity properties, such a specific global solver should also take advantage of the fact that most of the constraints in Problem (2.10) exhibit joint or, at least, related mathematical properties. For instance, the ECs (2.10b) in the LBP are usually based on derivatives of those terms that appear in the ICs, i.e., the chemical potential and the Gibbs free energy. Similarly, for CEOS, the ICs (5.2) represent the derivatives of the ECs which, again, motivates the need for a solver that is capable of identifying and exploiting those links.

Besides, it is interesting to note that a bilevel problem, such as Problem (2.10) is not directly amenable to classical maximum-likelihood estimation (MLE) or Bayesian inference since what is usually denoted as \( f(\theta) \) is not given explicitly in this case. The reason for this is that the predicted mole fractions in Problem (2.10) result from the minimization of one of the LLPs. This gives rise to its interpretation as a nonsmooth problem in the parameter space, where the variables in the upper-level objective function are obtained from black-box calls to certain solvers for the LLPs. Such a problem structure motivates an upper-bounding procedure of the bilevel algorithm complementing [110], in order to accelerate the convergence of the bilevel algorithm. It should be noted that the current upper-bounding procedure in [110] is based only on probing the bilevel-feasibility of a candidate solution.

In terms of optimization solvers, [26] and Chapter 5 also present numerical proofs that RGibbs through Aspen Plus [7] implements only local solvers. It would be interesting to perform a solver study including several hundreds of runs of RGibbs to determine the frequency of nonglobal solutions, with the purpose of assessing the impact of local solvers on today’s industrial process simulation results. Such studies could include REquil through Aspen Plus, as well as flash solvers of some popular regression tools, such as Aspen DRS [8] and the Gauss-Newton (GN) solver through DEHEMA DPP [1]. Also see Chapter 3 for the author’s recommendations on how to improve the performance of GN and DRS even without global optimization.

Finally, the reformulation of the GSIP in [107] to an SIP in Chapter 4 could be used to more efficiently process incomplete measurement data in BOARPET, also see Chapter 2 and [86].

Regarding parameter estimation for CEOS, in Chapter 5, a method is presented which applies the so-called \( \varphi - \varphi \) or symmetric approach. An extension to the \( \gamma - \varphi \) or asymmetric case is straightforward from a methodological point of view. Since the size of the sub-problems derived from Problem (2.10) in most cases, increases for \( \gamma - \varphi \), the numerical difficulties observed in Chapter 5 are likely to persist, or to even exacerbate. In particular, the extension includes the following steps: In Equation (J.5), the reference state of the
6.2 Future Work

chemical potential should be changed from “ideal gas” to “pure species at saturation”, calling for the fugacity coefficient of each pure species \(i\), \(\varphi_{\text{ois}}(T)\). Since \(\varphi_{\text{ois}}(T)\) is not a function of the parameters to be regressed, it can be calculated beforehand in the isothermal case. If, however, \(T\) is a variable during the regression, the sub-problems will include an additional variable for the molar volume of each pure species, along with the respective CEOS and root discrimination criteria. Besides, in the LBP, further parameters to be regressed arise, namely those of both the respective \(\Delta G^E\) and the CEOS model. Finally, the extension includes additional LLPs, due to an extra \(\Delta G\) curve resulting from the \(\Delta G^E\) model. To be specific, the regressed parameters are required to ensure the satisfaction of thermodynamic stability with respect to the \(\Delta G^E\) model and all of the solutions of the CEOS model. The asymmetric approach is, in most parts, implemented in BOARPET, though not fully tested.

Regarding parameter estimation in electrolytes and ionic liquids, the methods on reactive systems in Chapter 4 are fully expandable. Such methods are relevant to, e.g., LLE fluid systems which become single-phase upon addition of an electrolyte species, e.g., [91]. However, the strongly nonlinear terms in the eNRTL and related models [153, 151] lead to a slow convergence of BOARPET’s sub-solvers, if at all [166] which exacerbates their ready-to-use implementation.

There is also room for a more theoretical follow-up of [81, Equations 1 to 5] who derive the (R)TPC from a generic problem of a certain structure of which Problem (2.1) is only a special form. It would be an intriguing question whether there exist engineering problems, potentially beyond thermodynamics, to which this problem structure also applies. As an advantage, the problem could then be reformulated in a reduced variable space \(N - 1\), and the global minimizer could be conveniently found or validated by plotting only, even up to \(N = 3\), as opposed to \(N = 2\).
A Additional Remarks on Thermodynamic Stability

A.1 Lagrange Multipliers and Linear Independence of Constraints

Disclaimer: This appendix adopts Appendix A entitled “Lagrange multipliers and linear independence of constraints” from [63].

The global solution of the optimization problem with the embedded RTPC (Equation (2.5)) requires Lagrange multipliers with appropriate bounds. No multipliers are required for the TPC, nor the necessary conditions for equilibrium given in Section 2.1.2. The multipliers are bounded and unique iff LICQ is satisfied; it is a necessary criterion for the RTPC to hold, as this is based on KKT theory [81, 80, 154]. It should be noted that in a suitable variable space, the constraints (Equation (2.1b)) become linear and with the constraint qualification in [17, Proposition 3.3.7], it directly follows that the Lagrange multipliers are, at least, bounded. In general terms, however, LICQ should be considered; it is satisfied iff $A'$ has full rank [81]. In the following, we will briefly review some measures if the latter is not fulfilled.

Consider for instance, methanol synthesis from syngas. Setting up $A'$ in the space of chemical elements will result in a rank-deficiency of $A'$ [162, Example 16.3]. In order to alleviate this problem, the aforementioned authors and [155] recommend to reduce $A'$ by dropping one of the rows which causes linear dependence. On the other hand, [129] argue that the reaction invariants were simply selected inappropriately. For instance, using CO and $H_2$ instead of the chemical elements for methanol synthesis will allow for a full-rank $A'$. In other words, $A'$ depends on the choice of what is considered to be an “element” to be balanced. More generally, this can be any element which is invariant to reaction, and is not necessarily a chemical element. Ideally, reaction invariants are chosen such that $A' = I$, the identity matrix, leading to straightforward constraints.

In case the total molar amount is constant during the reaction, i.e., $\sum_i \nu_{i,rc} = 0$, $\forall rc$, [80] demonstrate rank-deficiency of $A'$. [81, 80] propose a reformulation of the atom balance constraints and a slightly reformulated version of the RTPC (Equation (2.5)) by introducing an additional Lagrange multiplier. Developing respective BLP regression formulations for the case of a constant total molar amount is not in the scope of this thesis and left for future work.

A.2 KKT First-Order Conditions of Smith et al.

Disclaimer: This appendix adopts Appendix B entitled “KKT first-order conditions of Smith et al.” from [63].
A.2 KKT First-Order Conditions of Smith et al.

We report the full equations system resulting from the KKT first-order conditions, cf. Problem (2.1) as reported in [154], in order to discuss the complementarity slackness conditions, according to

\[ n_{ph}^* \left( \mu_{i,ph}^* \left( x_{ph}^*, q \right) - \sum_j \lambda_j^* A_{ji}' \right) = 0, \quad \forall ph, i \]  
(A.1a)

\[ \theta_{ph}^* = \left( \sum_i x_{i,ph}^* \left( \mu_{i,ph}^* \left( x_{ph}^*, q \right) - \sum_j \lambda_j^* A_{ji}' \right) \right) \geq 0, \quad \forall ph \]  
(A.1b)

\[ \theta_{ph}^* n_{ph}^* = 0, \quad \forall ph \]  
(A.1c)

\[ \sum_{ph} n_{ph}^* \sum_i x_{i,ph}^* A_{ji}' - b_j = 0, \quad \forall j \]  
(A.1d)

\[ \sum_i x_{i,ph}^* - 1 = 0, \quad \forall ph \]  
(A.1e)

\[ \theta_{ph}^* \geq 0, \quad \forall ph. \]  
(A.1f)

Consequently, in the most general case of the RTPC, \( h^{u,1}(\cdot) \) in Problem (4.6) includes complementarity slackness conditions and thus, Problem (4.6) constitutes an MPEC in the upper level, subject to multiple NLPs in the lower level. By means of discretization methods, the program may be relaxed to an NLP [110]. Solving the NLP requires, e.g., regularization of the complementarity slackness conditions, formulation as penalty terms, reformulation as a mixed-integer nonlinear program (MINLP) or some other strategies, i.e., the relaxed program would have to be, at least, partly reformulated in order not to entail a violation of LICQ [18]. Alternatively, one may solve the relaxed program directly as an MPEC with solvers which support this as an additional feature, e.g., BARON [161]. However, in the case of regression, as opposed to, e.g., process simulations, \( Ph \) is commonly known a priori from experiments, eliminating the complementarity slackness conditions, cf. Equation (2.3).
B Additional Material on Convexity

Lemma 1 Let $n_{ph} \in \hat{N} \subseteq \mathbb{R}_{\geq 0}^N$ be the vector of the $N$ molar amounts of phase $ph$ and element of $n \in \hat{N} \subseteq \mathbb{R}_{\geq 0}^{N \times Ph}$. Consider now Problem (2.1) on the domain $\hat{N}$ for phase equilibrium, and suppose its feasibility and the existence of a minimum. The problem is strictly convex if the products $(\sum_i n_{i,ph}) \cdot \Delta G_{ph}(n_{ph})$ are continuous and strictly convex on $\hat{N}$.

Proof In the case of phase equilibrium only, we may rewrite Problem (2.1) to Problem (B.1) according to

$$\min_n \left( \Delta G(n) = \sum_{ph} \left( \sum_i n_{i,ph} \right) \Delta G_{ph}(n_{ph}) \right)$$

$$\sum_{ph} n_{i,ph} - n_i^0 = 0, \quad \forall i = 1, \ldots, N,$$

where $n_i^0 = \text{const.}$ is the molar amount of species $i$ in the feed. By assumption, Equation (B.1a) is a sum of strictly convex functions on $\hat{N}$ and thus, it is strictly convex in $n$. Similarly, Equation (2.2) is convex and it follows that the feasible domain of Problem (B.1) is convex in $n$. As a result, cf. e.g., [115], Problem (B.1) is strictly convex in $n$. □

Proposition 2 Let $n_{ph} \in \hat{N} \subseteq \mathbb{R}_{\geq 0}^N$ be the vector of the $N$ molar amounts of phase $ph$ and element of $n \in \hat{N} \subseteq \mathbb{R}_{\geq 0}^{N \times Ph}$. Consider now Problem (2.1) on the domain $\hat{N}$ for phase equilibrium, and suppose its feasibility, the existence of a minimum, i.e., $Ph \geq 1$, and that LICQ holds. If the sub-models of the Gibbs free energy $\Delta G_{ph}(x)$ are, at least, twice continuously differentiable and if the products $(\sum_i n_{i,ph}) \cdot \Delta G_{ph}(n_{ph})$ are strictly convex on $\hat{N}$, $\forall ph$, then Equation (2.10b) suffices to satisfy Equation (2.10d) for certain LLPs which we denote by 1 and 2 in the following. However, Equation (2.10b) does not suffice to satisfy Equation (2.10d) for a certain LLP we denote by 3.

Proof We first consider LLP 1, also see Figure 2.1a, followed by LLPs 2 and 3 related to Figure 2.1b and d, respectively. It should be noted that we do not wish to prove the convexity of the LLP but the satisfaction of the upper-level constraint on the respective lower-level optimal objective function value. Further, in the following, we do not give the lower-level constraints but only the lower-level objective functions. For the full formulation (as a GSIP), also see [107].

First, LLP 1 [20, 108, 107] encodes the well-known tangent plane distance function given by, e.g., Equation (2.5). By Lemma 1, Problem (B.1) is strictly convex, and its KKT first-order conditions (Equations (2.7)) become sufficient for the global minimizer of Problem (2.1), cf. e.g., [17]. By Theorem 2 it follows that any common tangent plane $\Theta(x)$ is a supporting hyperplane and thus, Equation (2.10b) is sufficient for

$$- f^{l,llp_1}(x^{u,llp_1}, q^u) \leq 0.$$

(B.2)
Next, for LLP 2 [20, 108, 107] propose Equation (4.5) which is a variation of the tangent plane distance function. It is well-known that for a strictly convex problem, the KKT first-order conditions become sufficient for a unique minimizer. By Theorem 2 the number of points of tangency is unique. Therefore, Equation (2.10b) is sufficient for
\[-f^{l,lp_2}(x^{u,lp_2}, q^u) \leq 0, \tag{B.3}\]
i.e., there exist no spurious phases. For LLP 3 [20, 108, 107] propose
\[f^{l,lp_3}(x^{l,lp_3}, q^u) = \Delta G_{ph_2}(x^{l,lp_3}, q^u) - \Delta G_{ph_1}(x^{l,lp_3}, q^u), \tag{B.4}\]
where $\Delta G_{ph_1}$ denotes the Gibbs free energy curve of the phase type that we wish to be stable, while $\Delta G_{ph_2}$ denotes the Gibbs free of the unstable phase type. (In the case of $Ph > 2$, LLP 3 considers all of the binary pairs.) We will prove this part of the proposition by giving a counterexample, also see Figure 2.1d, and by exploiting the well-known fact that the difference of two convex functions is not guaranteed to be convex.
Suppose different curvatures according to
\[
\left. \left( \frac{\partial^2 \Delta G_{ph_2}(q^u)}{\partial x^2} \right) \right|_{x^{l,lp_3}} - \left. \left( \frac{\partial^2 \Delta G_{ph_1}(q^u)}{\partial x^2} \right) \right|_{x^{l,lp_3}} < 0, \quad \forall x^{l,lp_3}, \tag{B.5}\]
and integrate for the specific choice that all of the integration constants are zero. Then,
\[\Delta G_{ph_2}(x^{l,lp_1}, q^u) - \Delta G_{ph_1}(x^{l,lp_3}, q^u) < 0, \tag{B.6}\]
and
\[-f^{l,lp_3}(x^{u,lp_3}, q^u) > 0, \tag{B.7}\]
irrespective of the convexities assumed, which completes the proof. \(\square\)

Remark: The assumption covers phase equilibrium only, as discussed in Section 2.3.1. Similar considerations are conceivable for chemical reaction equilibrium since
\[
\sum_{ph} \sum_i n_{i,ph} A'_{ji} - b_j = 0, \quad \forall j \tag{2.1b}\]
is linear in $n$ and the feasible region is, thus, convex. It should be noted that generally, $\Delta G_{ph,non-rec}(x, q^u) \neq G_{ph,rc}(x, q^u)$. In particular, if $\Delta G_{ph,non-rec}(x, q^u)$ is convex in $x$, so is $G_{ph,rc}(x, q^u)$ due to
\[G_{ph,rc}(x, q^u) = \sum_i x_{i,ph} \mu_i^0 + \Delta G_{ph,non-rec}(x, q^u), \tag{B.8}\]
where $\mu_i^0 = \text{const.}, \forall i$. However, this does not necessarily hold in terms of $n$ since the sum on the RHS then contains bilinear terms.
Case Study: THF/Water

Disclaimer: Contributions to this appendix: The author performed the regression in BOARPET, while Tjalf Hoffmann performed the regression with Gauss-Newton (DPP) using the files selected by the author.

Table C.1: Parameter bounds, initial and regressed values from Gauss-Newton (GN) and BOARPET through DEHEMA DPP, for the LLE of THF/water. For the model equations, see Equation (3.1).

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<th>Upper bound</th>
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<th>BOARPET</th>
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</tr>
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<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
<tr>
<td>C_{21}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
<tr>
<td>D_{12}</td>
<td>0.015366</td>
<td>-0.079334</td>
<td>0.079334</td>
<td>-0.023475</td>
<td>-0.044747</td>
</tr>
<tr>
<td>D_{21}</td>
<td>-0.0105149</td>
<td>-0.079334</td>
<td>0.079334</td>
<td>-0.014961</td>
<td>-0.0082734</td>
</tr>
</tbody>
</table>
D  Case Study: Butanole/Water

Disclaimer:  Contributions to this appendix: The author performed the regression in BOARPET, while Tjalf Hoffmann performed the regression with Gauss-Newton (DPP) using the files selected by the author.

Table D.1: Parameter bounds, initial and regressed values from Gauss-Newton (GN) and BOARPET through DECHEMA DPP, for the LLE of butanole/water. For the model equations, see Equation (3.1).

<table>
<thead>
<tr>
<th>Label</th>
<th>Initial</th>
<th>Lower bound</th>
<th>Upper bound</th>
<th>GN</th>
<th>BOARPET</th>
</tr>
</thead>
<tbody>
<tr>
<td>A_{12}</td>
<td>1.61894</td>
<td>-10</td>
<td>10</td>
<td>1.618944</td>
<td>-9.0901</td>
</tr>
<tr>
<td>A_{21}</td>
<td>1.98354</td>
<td>-10</td>
<td>10</td>
<td>1.98354</td>
<td>1.5972</td>
</tr>
<tr>
<td>B_{12}</td>
<td>289.59</td>
<td>-19482.5</td>
<td>19482.5</td>
<td>289.59</td>
<td>3382.8</td>
</tr>
<tr>
<td>B_{21}</td>
<td>139.84</td>
<td>-19482.5</td>
<td>19482.5</td>
<td>139.84</td>
<td>793.45</td>
</tr>
<tr>
<td>\hat{\alpha}_{12}</td>
<td>0.43621</td>
<td>0</td>
<td>1</td>
<td>0.43621</td>
<td>0.45280</td>
</tr>
<tr>
<td>\beta_{12}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
<tr>
<td>C_{12}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
<tr>
<td>C_{21}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
<tr>
<td>D_{12}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
<tr>
<td>D_{21}</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>not regressed</td>
<td></td>
</tr>
</tbody>
</table>
E Case Study: 2MTHF/Water

Disclaimer: This appendix adopts the measurement data of Maximilian Aigner (Table 2 in [59]; here E.1) and the results of the regressions performed by the author, given in Tables 3, 4, 6 and 7, as well as Appendices C and D entitled “Formulation of the Optimization Problem” and “Statistical Data Reported by Aspen DRS”, respectively, from [59].

E.1 Measurement Data and Regression Results for 2MTHF/Water

Table E.1: Experimental LLE data for temperature $T$, pressure $P$, and mole fraction of 2MTHF $x$ with standard uncertainty $u(x)$, for the system 2MTHF/water for both organic and aqueous phase (upper part chromatographic, lower part spectroscopic data).\(^a\)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (1 x 10^3 N m^-2)</th>
<th>$x$ org. phase (mol mol^-1)</th>
<th>$u(x)$ org. phase (mol mol^-1)</th>
<th>$x$ aq. phase (mol mol^-1)</th>
<th>$u(x)$ aq. phase (mol mol^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>22</td>
<td>0.81954</td>
<td>2.2534E-03</td>
<td>0.030537</td>
<td>5.8552E-05</td>
</tr>
<tr>
<td>303.15</td>
<td>35</td>
<td>0.82128</td>
<td>1.8823E-03</td>
<td>0.022920</td>
<td>2.3560E-05</td>
</tr>
<tr>
<td>313.15</td>
<td>43</td>
<td>0.82247</td>
<td>5.3430E-03</td>
<td>0.019512</td>
<td>9.1722E-04</td>
</tr>
<tr>
<td>323.15</td>
<td>61</td>
<td>0.80885</td>
<td>6.4385E-03</td>
<td>0.015832</td>
<td>1.5366E-03</td>
</tr>
<tr>
<td>333.15</td>
<td>67</td>
<td>0.81625</td>
<td>2.8997E-03</td>
<td>0.014731</td>
<td>5.5087E-04</td>
</tr>
<tr>
<td>343.15</td>
<td>96</td>
<td>0.79536</td>
<td>6.2987E-03</td>
<td>0.011415</td>
<td>3.5808E-04</td>
</tr>
<tr>
<td>293.15</td>
<td>22</td>
<td>0.84781</td>
<td>1.9211E-04</td>
<td>0.024922</td>
<td>2.6666E-04</td>
</tr>
<tr>
<td>303.15</td>
<td>35</td>
<td>0.83284</td>
<td>7.7358E-03</td>
<td>0.027406</td>
<td>4.6399E-05</td>
</tr>
<tr>
<td>333.15</td>
<td>67</td>
<td>0.82049</td>
<td>9.9091E-03</td>
<td>0.011802</td>
<td>4.9100E-04</td>
</tr>
<tr>
<td>363.15</td>
<td>194</td>
<td>0.83764</td>
<td>6.4971E-03</td>
<td>0.011732</td>
<td>4.5734E-05</td>
</tr>
<tr>
<td>393.15</td>
<td>471</td>
<td>0.80286</td>
<td>1.9035E-02</td>
<td>0.009517</td>
<td>4.3338E-04</td>
</tr>
<tr>
<td>423.15</td>
<td>965</td>
<td>0.77558</td>
<td>2.3849E-03</td>
<td>0.012269</td>
<td>4.3773E-04</td>
</tr>
</tbody>
</table>

\(^a\) Standard uncertainties $u$ are $u(T) = \pm 0.3 \text{ K}$ and $u(P) = \pm 1 \times 10^3 \text{ N m}^{-2}$. 
Table E.2: Settings and regressed values for the parameters of the NRTL model using Aspen DRS [8]. Each first line corresponds to 2MTHF/H$_2$O, each second to H$_2$O/2MTHF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regressed value</th>
<th>Initial value</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRTL/1</td>
<td>-31.4449</td>
<td>0</td>
<td>-1000</td>
<td>1000</td>
</tr>
<tr>
<td>NRTL/1</td>
<td>142.132</td>
<td>0</td>
<td>-1000</td>
<td>1000</td>
</tr>
<tr>
<td>NRTL/2</td>
<td>1079.95</td>
<td>0</td>
<td>-10000</td>
<td>10000</td>
</tr>
<tr>
<td>NRTL/2</td>
<td>-7712.72</td>
<td>0</td>
<td>-10000</td>
<td>10000</td>
</tr>
<tr>
<td>NRTL/3</td>
<td>0.405204</td>
<td>0.3</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>NRTL/5</td>
<td>5.26904</td>
<td>0</td>
<td>-1000</td>
<td>1000</td>
</tr>
<tr>
<td>NRTL/5</td>
<td>-19.8342</td>
<td>0</td>
<td>-1000</td>
<td>1000</td>
</tr>
</tbody>
</table>

Table E.3: Results of the regression of the LLE for temperature $T$ and mole fraction of 2MTHF $x$, for the system 2MTHF/water for both organic and aqueous phase. The regression is conducted in Aspen DRS [8] (upper part results for chromatographic, lower part for spectroscopic data).

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$x$ org. phase (mol mol$^{-1}$)</th>
<th>$x$ aq. phase (mol mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.09</td>
<td>0.84109</td>
<td>0.029953</td>
</tr>
<tr>
<td>303.15</td>
<td>0.83809</td>
<td>0.022867</td>
</tr>
<tr>
<td>313.04</td>
<td>0.83445</td>
<td>0.018456</td>
</tr>
<tr>
<td>323.12</td>
<td>0.83052</td>
<td>0.015505</td>
</tr>
<tr>
<td>333.05</td>
<td>0.82684</td>
<td>0.013550</td>
</tr>
<tr>
<td>343.21</td>
<td>0.82392</td>
<td>0.012200</td>
</tr>
<tr>
<td>293.64</td>
<td>0.84095</td>
<td>0.029470</td>
</tr>
<tr>
<td>302.74</td>
<td>0.83823</td>
<td>0.023090</td>
</tr>
<tr>
<td>333.32</td>
<td>0.82675</td>
<td>0.013507</td>
</tr>
<tr>
<td>363.14</td>
<td>0.83493</td>
<td>0.010770</td>
</tr>
<tr>
<td>393.13</td>
<td>0.79323</td>
<td>0.010493</td>
</tr>
<tr>
<td>423.18</td>
<td>0.7859</td>
<td>0.011865</td>
</tr>
</tbody>
</table>
**Table E.4:** Results of the regression of the LLE for temperature \( T \) and mole fraction of 2MTHF \( x \), for the system 2MTHF/water for both organic and aqueous phase. The regression is conducted in the regression tool BOARPET [109]. \( T \) is held constant during the regression.

<table>
<thead>
<tr>
<th>( T ) K</th>
<th>( x ) org. phase mol mol(^{-1})</th>
<th>( x ) aq. phase mol mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>293.15</td>
<td>0.82749</td>
<td>0.027312</td>
</tr>
<tr>
<td>303.15</td>
<td>0.82647</td>
<td>0.023360</td>
</tr>
<tr>
<td>313.15</td>
<td>0.82482</td>
<td>0.020224</td>
</tr>
<tr>
<td>323.15</td>
<td>0.82263</td>
<td>0.017697</td>
</tr>
<tr>
<td>333.15</td>
<td>0.82000</td>
<td>0.015633</td>
</tr>
<tr>
<td>343.15</td>
<td>0.81697</td>
<td>0.013926</td>
</tr>
<tr>
<td>363.15</td>
<td>0.80990</td>
<td>0.011295</td>
</tr>
<tr>
<td>393.15</td>
<td>0.79711</td>
<td>0.0086254</td>
</tr>
<tr>
<td>423.15</td>
<td>0.78204</td>
<td>0.0068679</td>
</tr>
</tbody>
</table>

**Table E.5:** Settings and regressed values for the parameters of the NRTL model using BOARPET [109]. 1 corresponds to 2MTHF, 2 to \( H_2O \). For the model equations, also see Equation (3.7).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regressed value</th>
<th>Initial value</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{12} )</td>
<td>1.8457</td>
<td>0</td>
<td>-2.5</td>
<td>10</td>
</tr>
<tr>
<td>( B_{12} )</td>
<td>-0.42682</td>
<td>0</td>
<td>-10</td>
<td>10</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( D_{12} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( E_{12} )</td>
<td>0.38551</td>
<td>0.2</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>( F_{12} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( A_{21} )</td>
<td>3.1987</td>
<td>0</td>
<td>-2.5</td>
<td>10</td>
</tr>
<tr>
<td>( B_{21} )</td>
<td>-3.5423</td>
<td>0</td>
<td>-10</td>
<td>10</td>
</tr>
<tr>
<td>( C_{21} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( D_{21} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### E.2 Formulation of the Optimization Problem

#### E.2.1 Problem Statement

Let the mole fraction \( x_{i,ph} \in [0,1] \) be an element of \( X = [0,1]^{N\times Ph} \), the molar phase fraction \( \Phi_{ph} \in [0,1] \) be an element of \( \Phi_i = [0,1]^{Ph} \), \( \Delta G \) be the molar Gibbs free energy of mixing, and \( \left( \frac{\partial^2 \Delta G}{\partial x \partial x} \right)_{x_{i,ph}} \) be the second-order derivative of the molar Gibbs free energy with respect to mole fraction at constant pressure and temperature, evaluated at \( x_{i,ph} \). For a feed denoted by 0, a stable split at constant pressure and temperature is given by the following problem

\[
\min_{\Phi,x} \sum_{ph} \Phi_{ph} \Delta G(x) \tag{E.1a}
\]
E.2 Formulation of the Optimization Problem

\[ \text{s.t. } \sum_{\phi} \Phi_{\phi} - 1 = 0 \quad (\text{E.1b}) \]

\[ \sum_{i=1}^{N} x_{i,\phi} - 1 = 0 \quad \forall \phi \quad (\text{E.1c}) \]

\[ \sum_{\phi} x_{i,\phi} \Phi_{\phi} - x_i^0 = 0, \quad \forall i = 1, \ldots, N. \quad (\text{E.1d}) \]

It should be noted that Problem (E.1) uses a different variable space than Problem (2.1). As required for optimization \( x_{i,\phi} \) and \( \Phi_{\phi} \) are elements of compact sets; this allows for some special solutions.

- \( \Phi_{\phi} = 0, \Phi_{\phi} = 1 \) for any \( \phi \) correspond to a solution with less than \( Ph \) phases.
- \( x_{i,1} = x_{i,II} = \ldots = x_{i,ph} \) for all \( i \) correspond to the trivial solution, i.e., a stable feed (single phase fluid).
- \( x_{i,ph} = 1 \) and \( x_{i,ph} = 0 \) for any \( i \) allows to reduce the dimension of the problem in terms of species in phase \( \phi \).
- \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{i,ph}} = 0 \) for any \( i, \phi \) corresponds to the limit of thermodynamic stability, cf. e.g., [162]. In order to prove that such a point is thermodynamically stable, higher-order derivatives need to be strictly positive. In this work, we do not consider any higher-order derivatives, yet we will draw some basic conclusions on the limit of stability for our specific problem. It should be noted that the problem formulation discussed in this thesis considers stable states excluding metastability.

For simplicity, in the following we neither allow for the trivial solution nor do we consider nonexisting species. In contrast to this general problem statement, [172] gives formulations for the specific cases of VLE, LLE and VLLE. Moreover, [172] reduces the number of variables by substituting \( \Phi \) in the objective with the help of the EC and by replacing one of the phase compositions using the KKT first-order conditions given in the following proof. However, this strategy is not pursued in this thesis for two reasons. First, in our case, the unconstrained problem will give inconveniently bulky expressions. In addition, the KKT first-order conditions give an explicit expression for one of the phase compositions only under certain thermodynamic assumptions which we consider too restrictive.

E.2.2 Sufficient Conditions for a Saddle Point

**Theorem 3** Consider Problem (E.1) at a point \((x_{1,1}, x_{1,II})\). Suppose that \((x_{1,1}, x_{1,II})\) satisfies the KKT first-order conditions of Problem (E.1) and that LICQ holds. Then,

\[ \text{sign } \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} = -\text{sign } \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}} \quad (\text{E.2}) \]

is a sufficient criterion for a saddle of Problem (E.1) at \((x_{1,1}, x_{1,II})\).
Proof Let us first consider the KKT first-order conditions of Problem (E.1). Based on \([17, 154, 81, 80]\) we derive

\[
\frac{\partial L}{\partial x_{1,1}} = \Phi \left( \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{1,1}} + \lambda \right) \not= 0
\]

\[
\Leftrightarrow \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{1,1}} = -\lambda.
\] (E.3)

The solution \(\Phi = 0\) is trivial (single-phase) and not considered further. It should be noted that this shows the physical significance of the Lagrangian multiplier, as has been pointed out before by \([106, 84]\), namely

\[-\lambda = \Delta \mu_{1,1}(x_{1,1}) - \Delta \mu_{2,1}(x_{1,1}),\] (E.4)

where \(\Delta \mu_{i,ph}\) is the chemical potential of species \(i\) in phase \(ph\), relative to the reference state “pure, real liquid”. The Lagrangian multiplier \(\lambda\) is the negative slope of the tangent at \(x_{1,1}\), i.e., the first derivative of \(\Delta G\) with respect to \(x_{i,ph}\). The relation of this derivative to the chemical potential is well-known from thermodynamics, cf. e.g., \([162]\),

\[
\Delta \mu_{i,ph}(x_{ph}) = \Delta G(x_{ph}) + \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{i,ph}} - \sum_{k=1}^{N-1} x_k \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{k,ph}},
\]

\[\forall i = 1, \ldots, N-1, \forall ph\]

\[
\Delta \mu_{N,ph}(x_{ph}) = \Delta G(x_{ph}) - \sum_{k=1}^{N-1} x_k \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{k,ph}}, \quad \forall ph.
\] (E.5)

Similarly,

\[
\frac{\partial L}{\partial x_{1,II}} = (1 - \Phi) \left( \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{1,II}} + \lambda \right) \not= 0
\]

\[
\Leftrightarrow \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{1,II}} = -\lambda.
\] (E.6)

The solution \(\Phi = 1\) is trivial (single-phase) and not considered further. The tangent at \(x_{1,II}\) is parallel to the tangent at \(x_{1,1}\) given by Equation (E.3), also see \([103]\),

\[
\left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{1,1}} = \left( \frac{\partial \Delta G}{\partial x} \right) \bigg|_{x_{1,II}}
\]

\[
\Leftrightarrow \Delta \mu_{1,1}(x_{1,1}) - \Delta \mu_{2,1}(x_{1,1}) = \Delta \mu_{1,II}(x_{1,II}) - \Delta \mu_{2,II}(x_{1,II}).
\] (E.7)

One solution of (E.7) is given by the equations system

\[
\Delta \mu_{1,1}(x_{1,1}) = \Delta \mu_{1,II}(x_{1,II})
\]

\[
\Delta \mu_{2,1}(x_{1,1}) = \Delta \mu_{2,II}(x_{1,II}), \quad (2.7)
\]

which is the isopotential criterion. The other is the trivial solution of same composition \(x_{1,1} = x_{1,II}\) and not considered further. Finally,

\[
\frac{\partial L}{\partial \Phi} = \Delta G(x_{1,1}) - \Delta G(x_{1,II}) + \lambda(x_{1,1} - x_{1,II}) \not= 0
\]
\[ \lambda = \frac{\Delta G(x_{1,1}) - \Delta G(x_{1,II})}{x_{1,1} - x_{1,II}}, \quad (E.8) \]

i.e., the secant is parallel to the tangents at \( x_{1,1} \) and \( x_{1,II} \). As a result of Equation (E.7) and (E.8), a necessary criterion for thermodynamic stability, alternatively to Equation (2.7), would be, e.g.,

\[ \Delta G(x_{1,1}) - \Delta G(x_{1,II}) = \Delta \mu_{2,1}(x_{1,1}) - \Delta \mu_{1,1}(x_{1,1}). \quad (E.9) \]

Furthermore, we conclude that both points \((x_{1,1}, \Delta G(x_{1,1}))\) and \((x_{1,II}, \Delta G(x_{1,II}))\) lie on the same tangent, resulting in a so-called double tangent. Considering that thermodynamic equilibrium is achieved at the global minimum of the Gibbs free energy, with the proof in [106], we can conclude that the double tangent is a supporting tangent. This is in essence the tangent plane criterion in [12]. Consequently, as an intermediate result, a point that satisfies isopotential, the slope of the secant and mass balance also satisfies the first-order conditions and is a stationary point, under the assumption of a suitable constraint qualification [81].

Let us consider now the Hessian \( H \in \mathbb{R}^{3 \times 3} \), i.e., the second-order derivatives of the Lagrangian with respect to the primal variables, and the basis of the null space \( P \in \mathbb{R}^{3 \times 2} \) according to Equations (E.10b), with linearly independent columns \( P_1 \in \mathbb{R}^3, P_1 \neq 0 \) and \( P_2 \in \mathbb{R}^3, P_2 \neq 0 \). In order to complete the KKT sufficient optimality conditions of a minimization problem, we consider the second-order conditions in addition to the aforementioned first-order conditions, cf. [17, 81],

\[ \nabla c^T P_1 = 0 \quad (E.10a) \]
\[ \nabla c^T P_2 = 0 \quad (E.10b) \]
\[ P^T HP \succeq 0, \quad (E.10c) \]

meaning that the projected Hessian \( P^T HP \) is positive definite.

For the EC \( c(x_{1,1}, x_{1,II}, \Phi) = x_{1,1}\Phi + x_{1,II}(1 - \Phi) - x^0 \), the first two conditions read

\[ (x_{1,1} - x_{1,II}, \Phi, -\Phi)P_i = 0, \quad i = 1, 2, \quad (E.11) \]

e.g.,

\[ P_1 = (0, 1, 1)^T \]
\[ P_2 = \left( 1, -\frac{(x_{1,1} - x_{1,II})}{\Phi}, 0 \right)^T. \quad (E.12) \]

For the second condition, we first write out the entries of the Hessian \( H \) for our specific case

\[ \frac{\partial^2 L}{\partial \Phi^2} = 0 \]
\[ \frac{\partial^2 L}{\partial(x_{1,1})^2} = \Phi \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} \]
\[ \frac{\partial^2 L}{\partial(x_{1,II})^2} = (1 - \Phi) \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}} \]
\[ \frac{\partial^2 L}{\partial \Phi \partial x_{1,1}} = \left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,1}} + \lambda \text{ KKT first-order } 0 \]
\[ \frac{\partial^2 L}{\partial \Phi \partial x_{1,II}} = -\left( \frac{\partial \Delta G}{\partial x} \right)_{x_{1,II}} - \lambda \text{ KKT first-order } 0 \]
\[ \frac{\partial^2 L}{\partial x_{1,1} \partial x_{1,II}} = 0. \quad (E.13) \]

It should be noted that the order of differentiation is irrelevant, and the resulting Hessian \( H \) is symmetric and given by
\[
H = \begin{bmatrix}
0 & 0 & 0 \\
0 & \Phi \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} & 0 \\
0 & 0 & (1 - \Phi) \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}}
\end{bmatrix} \quad (E.14)
\]

According to the last sufficient optimality condition let us determine the definiteness of the projected Hessian,
\[
P^T HP = \begin{bmatrix}
\Phi \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} + (1 - \Phi) \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}} & \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}}(x_{1,II} - x_{1,1}) \\
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} & \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}}(x_{1,II} - x_{1,1})^2
\end{bmatrix} \quad (E.15)
\]

following the criterion of Hurwitz. The determinant \( \det_1 \) of the sub-matrix reads
\[
\det_1 = \Phi \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} + (1 - \Phi) \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}}, \quad (E.16)
\]

while the determinant \( \det_2 \) of the full matrix reads
\[
\det_2 = \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}}(x_{1,II} - x_{1,1})^2 \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}}(1 - \Phi). \quad (E.17)
\]

As \( 0 < \Phi < 1 \) it is sign \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} \) and sign \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}} \) that decide on the definiteness of \( P^T HP \). A stationary point that satisfies
\[
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} > 0 \\
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,II}} > 0
\]
\[
\quad (E.18)
\]
yields \( \det_1 > 0 \) and \( \det_2 > 0 \), also see Equation (2.9). Consequently, \( P^T HP \) is positive definite and the point is a strict local minimum. Equation (E.18) in addition to the stationarity conditions is both a necessary and sufficient criterion for a strict local minimum. It should be noted that local convexity is a necessary criterion for a supporting tangent plane.

On the other hand, a stationary point that satisfies
\[
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_{1,1}} < 0
\]
E.2 Formulation of the Optimization Problem

\[ \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} < 0 \]  

(E.19)

yields \( \det_1 < 0 \) and \( \det_2 > 0 \). Consequently, \( P^T H P \) is negative definite. According to the KKT sufficient optimality conditions of a maximization problem such a point is a strict maximum. Equation (E.19) in addition to the stationarity conditions is both a necessary and sufficient criterion for a strict local maximum.

If, however, the stationary point satisfies

\[
\begin{align*}
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} & \neq 0 = \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} \\
\text{sign} \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} & = -\text{sign} \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}},
\end{align*}
\]

(E.20)

this yields \( \det_2 < 0 \). Consequently, \( P^T H P \) is indefinite irrespective of \( \det_1 \), and the point is a saddle which completes the proof. Equation (E.20) in addition to the stationarity conditions is a sufficient, yet not a necessary criterion for the existence of a saddle point, also see the discussion of the limit of thermodynamic stability in Appendix E.2.3.


E.2.3 Limit of Thermodynamic Stability

As a complement to Theorem 3, we will consider the limit of stability which corresponds to \( \left( \frac{\partial^3 \Delta G}{\partial x^3} \right) \bigg|_{x_{i,ph}} = 0 \), cf. e.g., [162]. In the following, we will discuss why, at least, one eigenvalue of the projected Hessian \( P^T H P \) becomes zero at the limit of stability. Since, however, in this case the criterion of Hurwitz is not applicable the eigenvalues will be examined.

1. If

\[
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} = 0 = \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}}
\]

(E.21)

the projected Hessian results in \( P^T H P = 0 \) and \( \lambda_{1,1} = 0 = \lambda_{1,II} \). It follows that the stationary point is a saddle.

2. If, however,

\[
\begin{align*}
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} & = 0 \\
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}} & \neq 0
\end{align*}
\]

(E.22)

the eigenvalues of the projected Hessian read

\[
\begin{align*}
\lambda_{1,1} & = 0 \\
\lambda_{1,II} & = (1 - \Phi) \left( \frac{\partial^2 \Delta G}{\partial x^2} \right) \bigg|_{x_{1,II}}.
\end{align*}
\]

(E.23)
If \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} > 0 \), the projected Hessian is positive semi-definite and the stationary point is a local minimum, yet not a strict local minimum. On the other hand, if \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} < 0 \), the projected Hessian is negative semi-definite and the stationary point is a local maximum, yet not a strict local maximum.

3. Similarly, if

\[
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} \neq 0
\]
\[
\left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} = 0
\] (E.24)

the eigenvalues of the projected Hessian read

\[
\lambda_{1,1} = \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} \frac{(x_{1,II} - x_{1,II})^2 + \Phi^2}{\Phi}
\]
\[
\lambda_{1,II} = 0.
\] (E.25)

If \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} > 0 \), the projected Hessian is positive semi-definite and the stationary point is a local minimum, yet not a strict local minimum. On the other hand, if \( \left( \frac{\partial^2 \Delta G}{\partial x^2} \right)_{x_1} < 0 \), the projected Hessian is negative semi-definite and the stationary point is a local maximum, yet not a strict local maximum.

To conclude, local optima which are not strict local optima correspond to the limit of thermodynamic stability. In addition, a saddle point may correspond to the limit of stability. At these stationary points, the Gibbs free energy may be even linear, as opposed to strictly convex or concave. A linear Gibbs free energy function can, for instance, correspond to the case of infinitely many coexisting phases with continuous compositions which cannot be a physical, stable state. In order to prove that stability is satisfied in the case of linearity, higher-order derivatives are required to be strictly positive, cf. e.g., [162].

### E.3 Statistical Data Reported by Aspen DRS

The standard deviation for the parameters reported by Aspen DRS is given in Table E.6. Aspen DRS reports the correlation matrix \( C \) for the parameters of the NRTL model, rows and columns as in Table E.2, according to

\[
C = \\
\begin{pmatrix}
1 & 0.037415 & 1 & -0.99572 & -0.053831 & 1 & -0.029284 & -0.99624 & 0.047743 & 1 & 0.057582 & -0.24993 & -0.053996 & 0.30079 & 1 & -0.99987 & -0.033561 & 0.99414 & 0.025192 & -0.056515 & 1 & -0.038762 & -0.99988 & 0.054788 & 0.99479 & 0.24025 & 0.034957 & 1
\end{pmatrix}
\]
Table E.6: Standard deviation for the parameters of the NRTL model, using Aspen DRS [8]. Each first line corresponds to 2MTHF/H₂O, each second to H₂O/2MTHF.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NRTL/1</td>
<td>25.886</td>
</tr>
<tr>
<td>NRTL/1</td>
<td>21.575</td>
</tr>
<tr>
<td>NRTL/2</td>
<td>1269.5</td>
</tr>
<tr>
<td>NRTL/2</td>
<td>1090.8</td>
</tr>
<tr>
<td>NRTL/3</td>
<td>0.001604</td>
</tr>
<tr>
<td>NRTL/5</td>
<td>3.7986</td>
</tr>
<tr>
<td>NRTL/5</td>
<td>3.1480</td>
</tr>
</tbody>
</table>
Case Study: 3MTHF/Water

Disclaimer: This appendix adopts the measurement data of Dominik Limper and the results of the regression performed by the author from [88], both to be found in “Data Regression of LLE 3-MTHF/Water”.

Table F.1: Experimental LLE data for temperature $T$, and mole fraction of 3MTHF $x$, for the system 3MTHF/water for both organic and aqueous phase.

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$x_{\text{org. phase}}$ mol mol$^{-1}$</th>
<th>$x_{\text{aq. phase}}$ mol mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>not measured</td>
<td>0.01979</td>
<td>[16]</td>
</tr>
<tr>
<td>293.15</td>
<td>not measured</td>
<td>0.02149</td>
<td>[16]</td>
</tr>
<tr>
<td>288.15</td>
<td>not measured</td>
<td>0.02321</td>
<td>[16]</td>
</tr>
<tr>
<td>283.15</td>
<td>not measured</td>
<td>0.02584</td>
<td>[16]</td>
</tr>
<tr>
<td>273.15</td>
<td>not measured</td>
<td>0.03453</td>
<td>[16]</td>
</tr>
<tr>
<td>273.15</td>
<td>0.8058</td>
<td>0.0104</td>
<td>[25]</td>
</tr>
<tr>
<td>298.15</td>
<td>not used</td>
<td>0.0200</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>not used</td>
<td>0.0482</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>not used</td>
<td>0.0405</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>not used</td>
<td>0.0433</td>
<td>[88]</td>
</tr>
<tr>
<td>283.15</td>
<td>0.8250</td>
<td>0.0579</td>
<td>[37]</td>
</tr>
<tr>
<td>293.15</td>
<td>0.8210</td>
<td>0.0378</td>
<td>[37]</td>
</tr>
<tr>
<td>303.15</td>
<td>0.8120</td>
<td>0.0286</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Table F.2: Experimental azeotropic data for temperature $T$, and mole fraction of 3MTHF $x$, for the system 3MTHF/water which are reported for the sake of completeness but not used in the regression. It should be noted that the azeotropic point depends on pressure which is not given. In order to include the azeotropic point in the regression, pressure and mole fractions of all coexisting phases are required.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$x$ at azeotrope mol mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>348.15</td>
<td>0.34644</td>
<td>[88]</td>
</tr>
</tbody>
</table>
Table F.3: Experimental single-phase data for temperature $T$, and mole fraction of 3MTHF $x$, for the system 3MTHF/water which are reported for the sake of completeness but not used in the regression.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$x$ single-phase mol mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>0.84485</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>0.92365</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>0.89082</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>0.90292</td>
<td>[88]</td>
</tr>
<tr>
<td>298.15</td>
<td>1.00000</td>
<td>[88]</td>
</tr>
</tbody>
</table>

Table F.4: Results of the regression of the LLE for temperature $T$ and mole fraction of 3MTHF $x$, for the system 3MTHF/water for both organic and aqueous phase. Regression is conducted with the regression tool BOARPET [109]. $T$ is held constant during the regression.

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$x$ org. phase mol mol$^{-1}$</th>
<th>$x$ aq. phase mol mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>0.81856</td>
<td>0.031375</td>
</tr>
<tr>
<td>283.15</td>
<td>0.81291</td>
<td>0.030053</td>
</tr>
<tr>
<td>288.15</td>
<td>0.81012</td>
<td>0.029456</td>
</tr>
<tr>
<td>293.15</td>
<td>0.80734</td>
<td>0.028895</td>
</tr>
<tr>
<td>298.15</td>
<td>0.80464</td>
<td>0.028369</td>
</tr>
<tr>
<td>303.15</td>
<td>0.80195</td>
<td>0.027873</td>
</tr>
<tr>
<td>323.15</td>
<td>0.79158</td>
<td>0.026153</td>
</tr>
</tbody>
</table>

Table F.5: Settings and regressed values for parameters of NRTL model using BOARPET [109]. 1 corresponds to 3MTHF, 2 to H$_2$O. For the model equations, see Equation (3.7). Valid for the temperature range 273.15 K $\leq T \leq$ 323.15 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regressed value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{12}$</td>
<td>-0.0055852 (regressed)</td>
</tr>
<tr>
<td>$B_{12}$</td>
<td>1.4351 (regressed)</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>0.0000 (fixed)</td>
</tr>
<tr>
<td>$D_{12}$</td>
<td>0.0000 (fixed)</td>
</tr>
<tr>
<td>$E_{12}$</td>
<td>0.15893 (regressed)</td>
</tr>
<tr>
<td>$F_{12}$</td>
<td>0.0000 (fixed)</td>
</tr>
<tr>
<td>$A_{21}$</td>
<td>3.7739 (regressed)</td>
</tr>
<tr>
<td>$B_{21}$</td>
<td>-2.2298 (regressed)</td>
</tr>
<tr>
<td>$C_{21}$</td>
<td>0.0000 (fixed)</td>
</tr>
<tr>
<td>$D_{21}$</td>
<td>0.0000 (fixed)</td>
</tr>
</tbody>
</table>
Disclaimer: This appendix adopts Appendices C and D entitled “KKT second-order sufficient conditions” and “Supplementary material”, respectively, from [63].

G.1 KKT Second-Order Sufficient Conditions

For the specific case of a binary single-phase reactive mixture with one reaction invariant, we extend the results in [81] (cf. Section 2.1.3) and [123] to sufficient conditions for a local minimum, maximum and saddle of the minimization of the Gibbs free energy, respectively.

**Proposition 3** Consider a binary single-phase reaction with one reaction invariant, molar fraction \( x \in (0, 1) \) and the molar Gibbs free energy function \( G(x) : (0, 1) \to \mathbb{R} \) which is, at least, twice continuously differentiable with respect to \( x \). Suppose that Problem (2.1) is feasible and that the stoichiometric matrix \( A' = (a'_1, a'_2) \), where \( a'_1, a'_2 \in \mathbb{R}_{>0} \), has full rank, i.e., LICQ holds [81], cf. Appendix A.1. Then, \( x^* \) satisfying the KKT first-order conditions is a local minimizer iff \( \left( \frac{\partial^2 G}{\partial x^2} \right)_{x^*} > 0 \), a local maximizer iff \( \left( \frac{\partial^2 G}{\partial x^2} \right)_{x^*} < 0 \), and a saddle iff \( \left( \frac{\partial^2 G}{\partial x^2} \right)_{x^*} = 0 \).

**Proof** Let us choose the variable space \((n, x)\) which is most appropriate for the RTPC. Then, the general formulation of the chemical reaction problem presented by [81] reduces to

\[
\begin{align*}
\min_{x,n} & \quad nG(x) \\
\text{s.t.} & \quad nx'a_1 + n(1 - x)a'_2 - b = 0,
\end{align*}
\]

where \( n \in \mathbb{R}_{>0} \). The Lagrangian reads

\[
L(x, n, \lambda) = nG(x) - \lambda (nx'a_1 + n(1 - x)a'_2 - b),
\]

where \( \lambda \in \mathbb{R} \) is the Lagrangian multiplier. From the KKT stationarity conditions [17], we obtain

\[
\frac{\partial L}{\partial n} = G(x) - \lambda ((a'_1 - a'_2)x + a'_2) = 0,
\]

noting that this is equivalent to \( G(x) - \Theta(x) = 0 \), cf. Equation (4.2), i.e., \( \Theta(x) \) and the Gibbs free energy curve coincide at a stationary point. Stationarity further yields

\[
\frac{\partial L}{\partial x} = n \left( \frac{\partial G}{\partial x} - \lambda (a'_1 - a'_2) \right) = 0,
\]
noting that with the above this is equivalent to $\frac{\partial G}{\partial x} = \frac{\partial \Theta}{\partial x}$. This confirms said proof \cite{81} in that at the stationary point, there exists a reactive tangent plane $\Theta(x)$ to the Gibbs free energy curve. It should be noted that the second part of the respective proof, i.e., $\Theta(x)$ is a supporting tangent plane, introduces a semi-infinite condition, cf. Equation (2.5). Therefore, it cannot be shown by means of KKT conditions alone due to their local nature. Using Equation (G.4) the Hessian $H \in \mathbb{R}^{2 \times 2}$ of the Lagrangian with respect to the primal variables reduces to

$$
H = \begin{pmatrix}
0 & 0 \\
0 & n\frac{\partial^2 G}{\partial x^2}
\end{pmatrix}.
$$

We determine now the basis of the null space $P \in \mathbb{R}^{2 \times 1}$, satisfying

$$(x(a_1' - a_2') + a_2', n(a_1' - a_2')) \cdot P = 0,$$

e.g., $P^T = \left(-\frac{n(a_1' - a_2')}{((a_1' - a_2')x + a_2')}, 1\right)$. The projected Hessian is, thus, given by

$$
P^T HP = n\frac{\partial^2 G}{\partial x^2}.
$$

Therefore, $\text{sign}\left(\frac{\partial^2 G}{\partial x^2}\right)$ is decisive for the definiteness of $P^T HP$. According to the second-order sufficient optimality conditions \cite{17} it follows that $x^*$ satisfying the KKT first-order conditions is a local minimizer iff $\left(\frac{\partial^2 G}{\partial x^2}\right)|_{x^*} > 0$, whereas it is a local maximizer iff $\left(\frac{\partial^2 G}{\partial x^2}\right)|_{x^*} < 0$, and a saddle iff $\left(\frac{\partial^2 G}{\partial x^2}\right)|_{x^*} = 0$. This completes said proofs \cite{81, 123} for the specific case of a binary single-phase reaction with one reaction invariant.

It should be noted that variable spaces other than $(n, x)$ to formulate Problem (G.1) are conceivable. For instance, the space $(n_1, n_2)$ is a straightforward choice which will give $P = \nu \in \mathbb{R}^{N \times (RC=MR)}$, the well-known stoichiometric matrix as the basis of the null space. This problem with $N$ variables and $MR = \text{rank}(A')$ linearly independent constraints can be interpreted as a reactive system with $N$ species, $MR$ reaction invariants and $RC$ chemical reactions \cite{155}. The specific cases of inert species $\nu_{i,rc} = 0$, $\forall rc$ \cite{129} and/or constant total mole numbers $\sum_i \nu_{i,rc} = 0$, $\forall rc$ \cite{80}, will result in $\nu$ being no longer basis of the null space and thus, are not covered in the present work.

**G.2 Regression and Simulation Results**

In this section, we report the results of the regression in detail with an accuracy of 4 significant digits, as well as the simulation results obtained with a chemical reactor model.

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### Table G.1: Results for Margules (Figures 4.1 to 4.4).

<table>
<thead>
<tr>
<th>Figure 4.1</th>
<th>Figure 4.2</th>
<th>Figure 4.3</th>
<th>Figure 4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB (LS)</td>
<td>0.0370</td>
<td>0.1742</td>
<td>0.2031</td>
</tr>
<tr>
<td>LBD</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.003094</td>
</tr>
<tr>
<td>A_0</td>
<td>0.1959</td>
<td>0.6520</td>
<td>-1.671</td>
</tr>
<tr>
<td>A_1</td>
<td>-200.0</td>
<td>-164.0</td>
<td>200.0</td>
</tr>
<tr>
<td>B_0</td>
<td>5.905</td>
<td>5.928</td>
<td>2.944</td>
</tr>
<tr>
<td>B_1</td>
<td>-190.7</td>
<td>-200.0</td>
<td>-200.0</td>
</tr>
</tbody>
</table>

### Table G.2: Simulation results of the chemical reactor model for Margules (Figures 4.1 to 4.4).

For Figure 4.3, we report the undesired global minimum in the row denoted by “Local min” for a more convenient presentation. It should be noted that within a tolerance of 3e-4 with respect to \( \frac{nG}{RT} \), these two minima can be considered equally global, while values of \( \xi \) do differ significantly.

<table>
<thead>
<tr>
<th>Type</th>
<th>Minimizer</th>
<th>Figure 4.1</th>
<th>Figure 4.2</th>
<th>Figure 4.3</th>
<th>Figure 4.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local min</td>
<td>( \left( \frac{nG}{RT} \right)^* )</td>
<td>1.046</td>
<td>see below</td>
<td>0.9072</td>
<td>see below</td>
</tr>
<tr>
<td></td>
<td>( x^* )</td>
<td>0.3764</td>
<td>see below</td>
<td>0.9153</td>
<td>see below</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{nG}{RT} \right)^* )</td>
<td>1.520</td>
<td>see below</td>
<td>0.9474</td>
<td>see below</td>
</tr>
<tr>
<td></td>
<td>( \xi^* )</td>
<td>0.4531</td>
<td>see below</td>
<td>0.04424</td>
<td>see below</td>
</tr>
<tr>
<td>Global min</td>
<td>( \left( \frac{nG}{RT} \right)^* )</td>
<td>0.9981</td>
<td>0.9980</td>
<td>0.9477</td>
<td>0.8540</td>
</tr>
<tr>
<td></td>
<td>( x^* )</td>
<td>0.9980</td>
<td>0.9980</td>
<td>0.578</td>
<td>0.5981</td>
</tr>
<tr>
<td></td>
<td>( \left( \frac{nG}{RT} \right)^* )</td>
<td>0.9981</td>
<td>0.9981</td>
<td>0.9477</td>
<td>0.8540</td>
</tr>
<tr>
<td></td>
<td>( \xi^* )</td>
<td>0.0009892</td>
<td>0.0009947</td>
<td>0.2675</td>
<td>0.2515</td>
</tr>
</tbody>
</table>

### Table G.3: Results for the case study presented in Figure 4.1.

<table>
<thead>
<tr>
<th>( k )</th>
<th>( T )</th>
<th>( x )</th>
<th>( n_{ph} )</th>
<th>( \lambda )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>295.0</td>
<td>0.1277</td>
<td>1.773</td>
<td>1.353</td>
<td>0.7735</td>
</tr>
<tr>
<td>2</td>
<td>296.0</td>
<td>0.1793</td>
<td>1.67</td>
<td>1.279</td>
<td>0.6959</td>
</tr>
<tr>
<td>3</td>
<td>297.0</td>
<td>0.2343</td>
<td>1.620</td>
<td>1.19</td>
<td>0.6203</td>
</tr>
<tr>
<td>4</td>
<td>298.0</td>
<td>0.2875</td>
<td>1.553</td>
<td>1.089</td>
<td>0.5534</td>
</tr>
<tr>
<td>5</td>
<td>299.0</td>
<td>0.3315</td>
<td>1.502</td>
<td>0.9818</td>
<td>0.5021</td>
</tr>
<tr>
<td>6</td>
<td>300.0</td>
<td>0.5194</td>
<td>1.316</td>
<td>0.8799</td>
<td>0.3163</td>
</tr>
<tr>
<td>7</td>
<td>301.0</td>
<td>0.5764</td>
<td>1.269</td>
<td>0.776</td>
<td>0.2687</td>
</tr>
<tr>
<td>8</td>
<td>302.0</td>
<td>0.6423</td>
<td>1.218</td>
<td>0.6801</td>
<td>0.2178</td>
</tr>
<tr>
<td>9</td>
<td>303.0</td>
<td>0.7146</td>
<td>1.166</td>
<td>0.5962</td>
<td>0.1665</td>
</tr>
<tr>
<td>10</td>
<td>304.0</td>
<td>0.9827</td>
<td>1.009</td>
<td>0.4926</td>
<td>0.008705</td>
</tr>
<tr>
<td>11</td>
<td>305.0</td>
<td>0.9351</td>
<td>1.034</td>
<td>0.4829</td>
<td>0.03352</td>
</tr>
</tbody>
</table>
### Table G.4: Results for the case study presented in Figure 4.2.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$T$ (K)</th>
<th>$x$ (mol mol$^{-1}$)</th>
<th>$n_{ph}$ (mol)</th>
<th>$\lambda$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>295.0</td>
<td>0.131</td>
<td>1.768</td>
<td>1.343</td>
<td>0.7684</td>
</tr>
<tr>
<td>2</td>
<td>296.0</td>
<td>0.175</td>
<td>1.702</td>
<td>1.280</td>
<td>0.7022</td>
</tr>
<tr>
<td>3</td>
<td>297.0</td>
<td>0.2250</td>
<td>1.633</td>
<td>1.204</td>
<td>0.6326</td>
</tr>
<tr>
<td>4</td>
<td>298.0</td>
<td>0.2807</td>
<td>1.562</td>
<td>1.117</td>
<td>0.5616</td>
</tr>
<tr>
<td>5</td>
<td>299.0</td>
<td>0.3422</td>
<td>1.490</td>
<td>1.022</td>
<td>0.4901</td>
</tr>
<tr>
<td>6</td>
<td>300.0</td>
<td>0.4217</td>
<td>1.407</td>
<td>0.9214</td>
<td>0.4068</td>
</tr>
<tr>
<td>7</td>
<td>301.0</td>
<td>0.4568</td>
<td>1.373</td>
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<td>0.3729</td>
</tr>
<tr>
<td>8</td>
<td>302.0</td>
<td>0.996</td>
<td>1.002</td>
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<td>0.002007</td>
</tr>
<tr>
<td>9</td>
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<td>0.9917</td>
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<td>0.004191</td>
</tr>
<tr>
<td>10</td>
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<td>0.9812</td>
<td>1.009</td>
<td>0.4919</td>
<td>0.009484</td>
</tr>
<tr>
<td>11</td>
<td>305.0</td>
<td>0.9405</td>
<td>1.031</td>
<td>0.4812</td>
<td>0.03068</td>
</tr>
</tbody>
</table>

### Table G.5: Results for the case study presented in Figure 4.3.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$T$ (K)</th>
<th>$x$ (mol mol$^{-1}$)</th>
<th>$n_{ph}$ (mol)</th>
<th>$\lambda$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>295.0</td>
<td>0.2961</td>
<td>1.543</td>
<td>0.3068</td>
<td>0.5431</td>
</tr>
<tr>
<td>2</td>
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<td>0.3099</td>
<td>1.527</td>
<td>0.3494</td>
<td>0.5269</td>
</tr>
<tr>
<td>3</td>
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<td>0.3279</td>
<td>1.506</td>
<td>0.3893</td>
<td>0.5062</td>
</tr>
<tr>
<td>4</td>
<td>298.0</td>
<td>0.3525</td>
<td>1.479</td>
<td>0.4251</td>
<td>0.4787</td>
</tr>
<tr>
<td>5</td>
<td>299.0</td>
<td>0.3887</td>
<td>1.440</td>
<td>0.4547</td>
<td>0.4402</td>
</tr>
<tr>
<td>6</td>
<td>300.0</td>
<td>0.4480</td>
<td>1.381</td>
<td>0.474</td>
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</tr>
<tr>
<td>7</td>
<td>301.0</td>
<td>0.5765</td>
<td>1.269</td>
<td>0.4739</td>
<td>0.2686</td>
</tr>
<tr>
<td>8</td>
<td>302.0</td>
<td>0.7827</td>
<td>1.122</td>
<td>0.4415</td>
<td>0.1219</td>
</tr>
<tr>
<td>9</td>
<td>303.0</td>
<td>0.7763</td>
<td>1.126</td>
<td>0.4055</td>
<td>0.1259</td>
</tr>
<tr>
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<td>304.0</td>
<td>0.7749</td>
<td>1.127</td>
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<td>0.1268</td>
</tr>
<tr>
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<td>305.0</td>
<td>0.7743</td>
<td>1.127</td>
<td>0.3335</td>
<td>0.1272</td>
</tr>
</tbody>
</table>
Table G.6: Results for the case study presented in Figure 4.4.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$T$</th>
<th>$x$</th>
<th>$n_{ph}$</th>
<th>$\lambda$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>K</td>
<td>mol mol$^{-1}$</td>
<td>mol</td>
<td>[]</td>
<td>[]</td>
</tr>
<tr>
<td>1</td>
<td>295.0</td>
<td>0.3050</td>
<td>1.533</td>
<td>0.2828</td>
<td>0.5325</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>0.3685</td>
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<td>0.4614</td>
</tr>
<tr>
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<td>0.4006</td>
<td>1.419</td>
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<td>0.4188</td>
</tr>
<tr>
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<td>300.0</td>
<td>0.4767</td>
<td>1.354</td>
<td>0.4336</td>
<td>0.3544</td>
</tr>
<tr>
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<td>1.252</td>
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</tr>
<tr>
<td>8</td>
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<td>0.7088</td>
<td>1.170</td>
<td>0.3983</td>
<td>0.1704</td>
</tr>
<tr>
<td>9</td>
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<td>0.7387</td>
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<td>0.3637</td>
<td>0.1503</td>
</tr>
<tr>
<td>10</td>
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<td>1.143</td>
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<td>0.1431</td>
</tr>
<tr>
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<td>0.7553</td>
<td>1.139</td>
<td>0.2922</td>
<td>0.1394</td>
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</table>

Table G.7: Results for NRTL (Figures 4.5 and 4.6).

<table>
<thead>
<tr>
<th></th>
<th>Figure 4.5</th>
<th>Figure 4.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>UBD (LS)</td>
<td>0.000003420</td>
<td>0.00003558</td>
</tr>
<tr>
<td>LBD</td>
<td>-0.00009658</td>
<td>-0.00006442</td>
</tr>
<tr>
<td>$A_{12}$ []</td>
<td>5.882</td>
<td>2.33</td>
</tr>
<tr>
<td>$F_{12}$ []</td>
<td>-31.47</td>
<td>82.07</td>
</tr>
<tr>
<td>$A_{21}$ []</td>
<td>-0.8540</td>
<td>-0.316</td>
</tr>
<tr>
<td>$F_{21}$ []</td>
<td>-46.21</td>
<td>-4.193</td>
</tr>
</tbody>
</table>

Table G.8: Simulation results of the chemical reactor model for NRTL (Figures 4.5 and 4.6).

<table>
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<th>Type</th>
<th>Minimizer</th>
<th>Figure 4.5</th>
<th>Figure 4.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Local min</td>
<td>($G_{RT}$)*</td>
<td>0.9850</td>
<td>see below</td>
</tr>
<tr>
<td></td>
<td>$x^*$</td>
<td>0.9873</td>
<td>see below</td>
</tr>
<tr>
<td></td>
<td>($nG_{RT}$)*</td>
<td>0.9913</td>
<td>see below</td>
</tr>
<tr>
<td></td>
<td>$\xi^*$</td>
<td>0.006403</td>
<td>see below</td>
</tr>
<tr>
<td>Global min</td>
<td>($G_{RT}$)*</td>
<td>0.6736</td>
<td>0.9341</td>
</tr>
<tr>
<td></td>
<td>$x^*$</td>
<td>0.5952</td>
<td>0.9455</td>
</tr>
<tr>
<td></td>
<td>($nG_{RT}$)*</td>
<td>0.8445</td>
<td>0.9603</td>
</tr>
<tr>
<td></td>
<td>$\xi^*$</td>
<td>0.2538</td>
<td>0.028</td>
</tr>
</tbody>
</table>
### Table G.9: Results for the case study presented in Figure 4.5.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$T$ (K)</th>
<th>$x$</th>
<th>$n_{ph}$ (mol)</th>
<th>$\lambda$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298.0</td>
<td>0.8494</td>
<td>1.081</td>
<td>0.5449</td>
<td>0.08142</td>
</tr>
<tr>
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<td>0.8762</td>
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<tr>
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</tr>
<tr>
<td>4</td>
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<td>0.9238</td>
<td>1.04</td>
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<td>0.03962</td>
</tr>
<tr>
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<td>302.0</td>
<td>0.9504</td>
<td>1.025</td>
<td>0.4974</td>
<td>0.02543</td>
</tr>
</tbody>
</table>

### Table G.10: Results for the case study presented in Figure 4.6.

<table>
<thead>
<tr>
<th>$k$</th>
<th>$T$ (K)</th>
<th>$x$</th>
<th>$n_{ph}$ (mol)</th>
<th>$\lambda$</th>
<th>$\xi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>298.0</td>
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<td>0.4423</td>
<td>0.08234</td>
</tr>
<tr>
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<td>0.4550</td>
<td>0.06609</td>
</tr>
<tr>
<td>3</td>
<td>300.0</td>
<td>0.9028</td>
<td>1.051</td>
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</tr>
<tr>
<td>4</td>
<td>301.0</td>
<td>0.9264</td>
<td>1.038</td>
<td>0.4737</td>
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</tr>
<tr>
<td>5</td>
<td>302.0</td>
<td>0.9455</td>
<td>1.028</td>
<td>0.4801</td>
<td>0.028</td>
</tr>
</tbody>
</table>

H Root Discrimination Criteria

Disclaimer: This appendix adopts Appendices A, B, and C entitled “First-order KKT conditions of Problem(5)”, “Analysis of root discrimination formulations in literature”, and “Cardan’s method”, respectively, from [62]. It should be noted that in this thesis, the author corrected the specification of those variables that are held constant during the differentiation in Equations (E.3) and (H.6). This did not affect the author’s results.

H.1 KKT First-Order Conditions

The Lagrangian of Problem (5.5) reads

\[ L(\lambda, \Phi, x_{1,1}, x_{1,II}, v_{II, r}, v_{II, r}) = \Phi \left( \Delta A(x_{1,1}, v_{I, r}) + P^0 v_{I, r} \right) + (1 - \Phi) \left( \Delta A(x_{1,II}, v_{II, r}) + P^0 v_{II, r} \right) + \lambda_1 (x_{1,1} \Phi + x_{1,II} (1 - \Phi) - x_0^0) - \lambda_2 \Phi - \lambda_3 (1 - \Phi), \]  

(H.1)

where \( \lambda \in \mathbb{R}^3 \) is the vector of the Lagrangian multipliers. Let now \( \left( \frac{\partial \Delta A}{\partial v} \right) \bigg|_{x_{ph},v_{ph,r}} \) denote the first-order derivative of \( \Delta A(x_{ph}, v_{ph,r}) \) of a binary mixture with respect to \( v \), while holding \( T \) and the variable mentioned at the respective juncture constant, evaluated at \( (x_{ph}, v_{ph,r}) \). First, consider the KKT first-order conditions with respect to molar volume given by

\[ 0 \leq \left( - P \big|_{x_{1,1},v_{I, r}} + P^0 \right) \perp \Phi > 0. \]  

(5.8)

In case \( \Phi > 0 \) it follows that the CEOS is satisfied as intended by reformulating Problem (5.4) to Problem (5.5) according to

\[ 0 = - P \big|_{x_{1,1},v_{I, r}} + P^0. \]  

(H.2)

On the other hand, if \( \Phi = 0 \) cubic equality is relaxed according to Equation (5.8). (It should be noted that in this particular case, the complementarity condition results from an EC as opposed to an IC, where the solution \( \Phi = 0 \) implies vanishing of a phase.) Similarly,

\[ \frac{\partial L}{\partial v_{II, r}} = (1 - \Phi) \left( \frac{\partial \Delta A}{\partial v} \right) \bigg|_{x_{1,II},v_{II, r}} + P^0 \right) \perp 0 \]  

(H.2)
\[ \Leftrightarrow 0 \leq \left( -P|_{x_1,II,v_{II,r}} + P^0 \right) \perp (1 - \Phi) \geq 0. \quad (H.3) \]

Equation (5.8) together with (H.3) yields
\[ 0 \leq \left( -P|_{x_1,II,v_{II,r}} + P^0 \right) \perp \left( -P|_{x_1,II,v_{II,r}} + P^0 \right) \geq 0, \quad (H.4) \]

since, at least, one phase must exist. On the other hand, if both phases exist, we may apply Equation (H.2) to both phases and obtain
\[ P|_{x_1,I,v_{I,r}} = P|_{x_1,II,v_{II,r}}, \quad (H.5) \]

which yields the mechanical equilibrium, and implies a double-tangent to the surface of the Helmholtz free energy with respect to molar volume. According to Equations (5.8), (H.3) and (H.4) mechanical equilibrium may be relaxed if any of the phases vanishes.

Let us now consider the derivatives of the Lagrangian with respect to composition, while holding the other optimization variables including \( v_{ph,r} \) constant, i.e.,
\[ \frac{\partial L}{\partial x_{1,I}} = \Phi \left( \left( \frac{\partial \Delta A}{\partial x} \right)|_{x_1,I,v_{I,r}} + \lambda_1 \right) = 0 \]
\[ \Leftrightarrow 0 \leq \left( \left( \frac{\partial \Delta A}{\partial x} \right)|_{x_1,I,v_{I,r}} + \lambda_1 \right) \perp \Phi \geq 0. \quad (E.3) \]

Similarly,
\[ \frac{\partial L}{\partial x_{1,II}} = (1 - \Phi) \left( \left( \frac{\partial \Delta A}{\partial x} \right)|_{x_1,II,v_{II,r}} + \lambda_1 \right) = 0 \]
\[ \Leftrightarrow 0 \leq \left( \left( \frac{\partial \Delta A}{\partial x} \right)|_{x_1,II,v_{II,r}} + \lambda_1 \right) \perp (1 - \Phi) \geq 0. \quad (H.6) \]

Considering first the case of \( \Phi \in (0, 1) \), it follows from Equations (E.3) and (H.6) that the tangent at \( x_{1,II} \) is parallel to the tangent at \( x_{1,I} \). Noting that for a binary mixture at \( T, V = \text{const.} \),
\[ \left( \frac{\partial \Delta A}{\partial x} \right)|_{x_{1,ph},v_{ph,r}} = \Delta \mu_{1,ph}(x_{1,ph}, v_{ph,r}) - \Delta \mu_{2,ph}(x_{1,ph}, v_{ph,r}), \quad (H.7) \]

we obtain
\[ \Delta \mu_{1,1}(x_{1,I}, v_{I,r}) = \Delta \mu_{1,II}(x_{1,II}, v_{II,r}) \]
\[ \Delta \mu_{2,1}(x_{1,I}, v_{I,r}) = \Delta \mu_{2,II}(x_{1,II}, v_{II,r}), \quad (2.7) \]

which is the isopotential criterion. On the other hand, if \( \Phi \in \{0, 1\} \), isopotential is relaxed according to Equations (E.3) and (H.6).

Finally, let us take the derivatives with respect to phase fraction \( \Phi \) according to
\[ \frac{\partial L}{\partial \Phi} = \Delta A(x_{1,I}, v_{I,r}) + P^0 v_{I,r} + \lambda_1 x_{1,I} \]
\[-\Delta A(x_{1,\text{II}}, v_{\text{II},r}) - P^0 v_{\text{II},r} - \lambda_1 x_{1,\text{II}} - \lambda_2 + \lambda_3 = 0. \quad (H.8)\]

Rearranging yields

\[0 = \Delta A(x_{1,\text{I},v_{\text{I},r}}) - \Delta A(x_{1,\text{II},v_{\text{II},r}}) + P^0 (v_{\text{I},r} - v_{\text{II},r}) + \lambda_1 (x_{1,\text{I}} - x_{1,\text{II}}) - \lambda_2 + \lambda_3. \quad (H.9)\]

Finally, for dual feasibility and the complementarity condition, it follows

\[0 \leq \lambda_2 \perp \Phi \geq 0 \quad (H.10a)\]
\[0 \leq \lambda_3 \perp (1 - \Phi) \geq 0. \quad (H.10b)\]

If a phase vanishes, \(P^0\) and \(\lambda_1\) in Equation (H.9) will not necessarily give the first-order derivatives of \(\Delta A(x_{\text{ph},v_{\text{ph},r}})\) according to Equations (H.2) and (E.3). In addition, either \(\lambda_2 > 0\) or \(\lambda_3 > 0\) due to Equation (H.10). Hence, Equation (H.9) cannot be a tangent to the surface of the Helmholtz free energy if a phase vanishes. This can be considered a relaxation of the tangent plane criterion. On the other hand, in case both phases exist, with Equations (H.2), (E.3) and (H.10), Equation (H.9) results in

\[
\Delta A(x_{1,\text{II},v_{\text{II},r}}) - \Delta A(x_{1,\text{I},v_{\text{I},r}}) = \left( \frac{\partial \Delta A}{\partial x} \right)_{x_{1,\text{I},v_{\text{I},r}}} (x_{1,\text{II}} - x_{1,\text{I}}) + \left( \frac{\partial \Delta A}{\partial v} \right)_{x_{1,\text{I},v_{\text{I},r}}} (v_{\text{II},r} - v_{\text{I},r}),
\]

which is a double-tangent plane to the surface of the Helmholtz free energy with respect to both composition and molar volume. It should be noted that this result cannot be obtained from the unconstrained problem presented by [102].

Altogether, a stationary point of Problem (5.5) with both phases present satisfies cubic equality, isopotential and the mechanical equilibrium. Considering that the global minimum of Problem (5.5) gives a stable state, we can follow the proof in [106] to conclude that the tangent plane with respect to \(\Delta A(x_{\text{ph},v_{\text{ph},r}})\) is a supporting tangent plane, since else there would exist another tangent to further reduce the thermodynamic potential \((\Delta G(x_{\text{ph},v_{\text{ph},r}})\) or \(\Delta A(x_{\text{ph},v_{\text{ph},r}})\)). This results in a tangent plane criterion in terms of \(\Delta A(x_{\text{ph},v_{\text{ph},r}})\). On the other hand, if a phase vanishes, cubic equality, along with the phase and mechanical equilibrium, are relaxed simultaneously, as these all depend on \(\Phi\).

### H.2 Analysis of Root Discrimination Formulations in the Literature

In the main part, root discrimination criteria from the literature are listed. In this section, these are reviewed and compared to Problem (5.4) and Criterion (5.1). For the last two examples from the literature, the comparison includes several case studies, and the results are discussed in Appendix H.2.3 and Section 5.2.4, in the main part. For the sake of completeness we first consider a criterion which is not explicitly taken from the literature but might be a suitable starting point, as it seems to be the most basic one.
H.2 Analysis of Root Discrimination Formulations in the Literature

H.2.1 Criterion Based on Simple Inequalities

As a basic criterion for distinguishing roots \(v_{ph,1}, v_{ph,3}\) and the intermediate root \(v_{ph,2}\) of a CEOS consider

\[
\begin{align*}
    f_{ceos}(x_{ph}, v_{ph,1}) &= 0 & \text{(H.11a)} \\
    f_{ceos}(x_{ph}, v_{ph,2}) &= 0 & \text{(H.11b)} \\
    f_{ceos}(x_{ph}, v_{ph,3}) &= 0 & \text{(H.11c)} \\
    v_{ph,1} &< v_{ph,2} < v_{ph,3}. & \text{(H.11d)}
\end{align*}
\]

The advantage of this criterion is its simplicity. On the other hand, compared to Criterion (5.1) and root discrimination based on thermodynamic stability, the drawbacks are: i) Three volume variables are required, as opposed to two for Criterion (5.1) and one for Problem (5.4). With two volume variables only, it would not be clear which real root to match each with. ii) Moreover, strict inequalities are problematic for constraints in optimization since the feasible set is not guaranteed to be closed and hence, a solution may not exist which is why most optimization solvers and modeling environments do not allow such strict inequalities. By introducing a tolerance \(\epsilon\) one can rewrite Criterion (H.11) to closed inequalities, yet this will render the third drawback more pronounced. iii) Most importantly, the criterion is applicable only to the case of three distinct real roots; else potentially valid solutions \((x_{ph}, v_{ph,r})\) will be cut off due to the strict inequality. Finally, in contrast to Criterion (H.11), Problem (5.4) satisfies the sufficient condition for thermodynamic stability.

H.2.2 Criterion of Poling et al.

[136] present a root discrimination criterion that is based on isothermal compressibility \(\beta\) (not to be confused with compressibility factor \(Z = \frac{Pv}{RT}\)), in order to assign phase types to volume roots in CEOS models. The state is characterized liquid-like or vapor-like depending on the values of \(\beta\) and \(P\) according to

\[
\begin{align*}
    \text{liquid: } &\beta < 0.005 \text{ atm}^{-1} \approx 4.93 \times 10^{-8} \text{ m}^2\text{N}^{-1} & \text{(H.12a)} \\
    \text{vapor: } &0.9 < \beta P < 3. & \text{(H.12b)}
\end{align*}
\]

While this root discrimination criterion is simple and straightforward to implement, Criterion (5.1) and Problem (5.4) offer several advantages: The feasibility of Criterion (5.1) and Problem (5.4) is always ensured, whereas Criterion (H.12) is not guaranteed to hold as discussed in [136]. Furthermore, thermodynamic stability, even the necessary condition in Equations (5.9b) and (5.9d), is not guaranteed to be satisfied by Criterion (H.12). In contrast, Problem (5.4) satisfies the sufficient condition for thermodynamic stability, and Criterion (5.1) satisfies a necessary condition. Furthermore, Criterion (H.12) is not guaranteed to uniquely classify the roots. It may as well be satisfied by both the intermediate and the liquid-like root, or even by all three real roots, although this is highly unlikely. The vapor-like case can be discussed analogically. In contrast, Problem (5.4) distinguishes the stable root from the unstable ones, and Criterion (5.1) discriminates between the roots according to second-order derivatives [83].

It should be noted that [136] presume that \(\left(\frac{\partial f_{ceos}}{\partial \nu}\right)_{x_{ph},v_{ph,r}} = 0\) be the point between the single-real-root region and the multiple-real-root region (with potentially coinciding roots), see Appendix H.3 for a formal confirmation.
H.2.3 Criterion of Kamath et al.

[83] develop a criterion that discriminates between the roots by assigning phase types, similar to [136]. It is based on pure calculus, and refers to any cubic equation irrespective of thermodynamics. [83] give proof that a combination of the first- and second-order derivative of a cubic equation uniquely characterizes a real root. In addition, vapor is assigned the maximal root and liquid the minimal root ($Z_1 \geq Z_2 > Z_3$). They then prove that for the maximal root

$$\left. \left( \frac{\partial f_{\text{ceos}}}{\partial Z} \right) \right|_{x_{\text{ph}}, Z_{\text{ph},1}} \geq 0 \quad (H.13a)$$

$$\left. \left( \frac{\partial^2 f_{\text{ceos}}}{\partial Z^2} \right) \right|_{x_{\text{ph}}, Z_{\text{ph},1}} \geq 0, \quad (H.13b)$$

whereas for the minimal root

$$\left. \left( \frac{\partial f_{\text{ceos}}}{\partial Z} \right) \right|_{x_{\text{ph}}, Z_{\text{ph},3}} \geq 0 \quad (H.14a)$$

$$\left. \left( \frac{\partial^2 f_{\text{ceos}}}{\partial Z^2} \right) \right|_{x_{\text{ph}}, Z_{\text{ph},3}} \leq 0. \quad (H.14b)$$

On the other hand, the intermediate root satisfies

$$\left. \left( \frac{\partial f_{\text{ceos}}}{\partial Z} \right) \right|_{x_{\text{ph}}, Z_{\text{ph},2}} \leq 0, \quad (H.15)$$

which is consistent with Equations (5.9b) and (5.9d). The criterion allows for distinguishing the case of three isolated real roots from the cases of exactly two and three coinciding real roots, respectively. In the case of three real roots the criterion can distinguish the minimal from the maximal and the intermediate real root.

It should be noted that [83] redefine vapor and liquid according to Equations (H.13) and (H.14). Since a phase is a thermodynamically stable system, phase types cannot be assigned to CEOS roots and thus, states, without proving thermodynamic stability. However, this is what [83, Definitions 2 and 3] seem to suggest. Although the core of their proof is correct, the difficulty in applying the criterion, in our opinion, thus, lies in their conclusions on thermodynamics including terminology (“vapor”, “liquid”). While the criterion does not guarantee stability, it satisfies the necessary condition for stability. This is similar to Criterion (5.1), yet different from Problem (5.4) which satisfies the sufficient condition for stability.

H.3 Cardano’s Method

Cardano’s method gives a criterion to distinguish single-real-root from multiple-real-root solutions of a cubic equation by means of a discriminant $D$, as well as providing the analytical roots. We will first introduce the basic implications following from this method, cf. e.g., [119, 40]. Let $b, c, d \in \mathbb{R}$ be coefficients, $\hat{v}_r \in \mathbb{C}$ be a variable and $f_{\text{ceos}}(\hat{v}_r), f_{\text{ceos}} : \mathbb{C} \to \mathbb{C}$ be a cubic and thus, twice continuously differentiable function of the form

$$f_{\text{ceos}}(\hat{v}_r) = \hat{v}_r^3 + b\hat{v}_r^2 + c\hat{v}_r + d. \quad (H.16)$$
Let now \( v_r \in \mathbb{C} \) be a root satisfying \( f_{\cos}(v_r) = 0 \), and define \( p \in \mathbb{R} \) and \( q \in \mathbb{R} \) according to

\[
p := \frac{2b^3 - 9bc + 27d}{54}, \quad q := \frac{b^2 - 3c}{9}.
\]

(H.17)

Let further \( f'_{\cos}(\hat{v}_r), f''_{\cos} : \mathbb{C} \to \mathbb{C} \) and \( f'_{\cos}(\hat{v}_r), f''_{\cos} : \mathbb{C} \to \mathbb{C} \) be first- and second-order derivative of \( f_{\cos}(\hat{v}_r) \) with respect to \( \hat{v}_r \), respectively. It should be noted that the derivatives are continuous due to twice continuous differentiability of \( f_{\cos}(\hat{v}_r) \). Finally, let \( D_1, D \in \mathbb{R} \) denote some discriminants. There is no uniform definition of the discriminant in the literature. A common one seems to be

\[
D_1 := c^2b^2 - 4db^3 - 4c^3 + 18dbc - 27d^2.
\]

(H.18)

In this work, we use,

\[
D := p^2 - q^3,
\]

noting that

\[
D_1 = -108D.
\]

(H.20)

Then, according to Cardano’s method,

- if \( D > 0 \): \( f_{\cos}(\hat{v}_r) \) has only one real root.
- if \( D < 0 \): \( f_{\cos}(\hat{v}_r) \) has three distinct real roots.
- if \( D = 0 \): \( f_{\cos}(\hat{v}_r) \) has three real roots, some of which are coinciding.

In the following, we will use Cardano’s method, in order to give a formal proof of the conjecture in [136] and [46].

**Proposition 4** Let \( f_{\cos}(\hat{v}_r) \) and \( f'_{\cos}(\hat{v}_r) \) denote the functions as introduced above. Then, \( f'_{\cos}(\hat{v}_r) = 0 \) is the transition between the single-real-root region and the multiple-real-root region (with potentially coinciding roots).

**Proof** We first derive a preliminary result given by Equation (H.26) that will be the key relation for this proof. The basic idea is to relate the stationary values, cf. e.g., [32], to Cardano’s method. Consider the stationary values \( v_{\text{stat},1} \in \mathbb{C} \) and \( v_{\text{stat},2} \in \mathbb{C} \) of \( f_{\cos} \) satisfying

\[
f'_{\cos}(v_{\text{stat},r}) = 3v_{\text{stat},r}^2 + 2bv_{\text{stat},r} + c = 0, \quad r = 1, 2,
\]

(H.21)

and

\[
|v_{\text{stat},2}| \leq |v_{\text{mid}}| \leq |v_{\text{stat},1}|
\]

(H.22)

for some \( v_{\text{mid}} \in \mathbb{C} \). Using Equation (H.17) for the stationary values we obtain

\[
v_{\text{stat},1} = + \sqrt{q} - \frac{b}{3}
\]

\[
v_{\text{stat},2} = - \sqrt{q} - \frac{b}{3},
\]

(H.23)
Evaluate now \( f_{\cos}(\hat{\nu}_r) \) at the stationary values. After rearranging and using Equation (H.17) this yields

\[
\begin{align*}
\frac{f_{\cos}(v_{\text{stat},1})}{f_{\cos}(v_{\text{stat},2})} &= -2q\sqrt{q} + 2p \\
\frac{f_{\cos}(v_{\text{stat},2})}{f_{\cos}(v_{\text{stat},1})} &= 2q\sqrt{q} + 2p.
\end{align*}
\]

Noting that with

\[
\frac{f''_{\cos}(\hat{\nu}_r)}{f_{\cos}(\hat{\nu}_r)} = 6\hat{\nu}_r + 2b,
\]

it follows that \( v_{\text{stat},1} \) satisfies the necessary conditions for a minimum value, while \( v_{\text{stat},2} \) satisfies the necessary conditions for a maximum value. Note further that for a cubic equation of the form of \( f_{\cos}(\hat{\nu}_r) \) we can conclude from Equation (H.25) that the function is convex with respect to \( \hat{\nu}_r \) for \( \hat{\nu}_r \to \infty \), whereas it is concave for \( \hat{\nu}_r \to -\infty \), giving the shape depicted in, e.g., Figure H.1. Now, with Equation (H.19), it follows from Equation (H.24) after some rearranging that

\[
\frac{f_{\cos}(v_{\text{stat},1})}{f_{\cos}(v_{\text{stat},2})} = 4(p^2 - q^3) = 4D.
\]

We now show that \( f_{\cos}(\hat{\nu}_r) \) exhibits three real roots, some of which coincide, if \( f'_{\cos}(\hat{\nu}_r) = 0 \). According to Cardano’s method \( D = 0 \) in the case of coinciding roots. It follows with Equation (H.26)

\[
\frac{f_{\cos}(v_{\text{stat},1})}{f_{\cos}(v_{\text{stat},2})} = 0.
\]

Consequently, at least, one stationary value \( v_{\text{stat},r} \) is a root to \( f_{\cos}(\hat{\nu}_r) \). The case of exactly one stationary value being a root to \( f_{\cos}(\hat{\nu}_r) \) is illustrated in Figure H.1.

For the sake of completeness we also briefly discuss \( q \leq 0 \). First, if \( q < 0 \) \( v_{\text{stat},1}, v_{\text{stat},2} \in \mathbb{C} \) according to Equation (H.23). This implies that \( f_{\cos}(\hat{\nu}_r) \) is strictly monotonic in \( \mathbb{R} \) and only a single real root exists, cf. Figure H.2. According to Equation (H.26) it follows \( D \geq 0 \) and hence, Cardano’s method even applies to the region where no stationary value \( v_{\text{stat},r} \in \mathbb{R} \) exists.

Second, consider the case of three coinciding roots. From

\[
f_{\cos}(v_{\text{stat},1}) = f_{\cos}(v_{\text{stat},2}),
\]
it follows with Equation (H.24) that \( q = 0 \). Consequently, from Equation (H.23)
\[
v_{\text{stat},1} = v_{\text{stat},2}, \tag{H.29}
\]
i.e., the stationary values coincide, and \( f_{\text{ceos}}(v_r) \) is monotonic. With continuity according to Equation (H.22), we obtain,
\[
v_{\text{stat},2} = v_{\text{mid}} = v_{\text{stat},1}, \tag{H.30}
\]
i.e., all of the three roots coincide, cf. Figure H.3. Note that with Equation (H.25), this agrees with the inflection point, i.e.,
\[
f''_{\text{ceos}}(v_{\text{stat},r}) = 0. \tag{H.31}
\]
As a first intermediate result, we obtain, thus, the following: If \( D = 0 \), that is, there are three real roots, some of which coincide according to Cardano’s method, we have \( f_{\text{ceos}}(v_r) = f'_{\text{ceos}}(v_r) = 0 \), i.e., \( v_r \) is a root to both \( f_{\text{ceos}}(\hat{v}_r) \) and \( f'_{\text{ceos}}(\hat{v}_r) \).

We finally show that \( f_{\text{ceos}}(\hat{v}_r) \) exhibits a single real root or three distinct real roots if \( f'_{\text{ceos}}(\hat{v}_r) \neq 0 \). In the case of a single-real-root solution \( D > 0 \) according to Cardano’s method. It follows with Equation (H.26) that
\[
f_{\text{ceos}}(v_{\text{stat},1}) \cdot f_{\text{ceos}}(v_{\text{stat},2}) > 0, \tag{H.32}
\]
which is illustrated in Figure H.4. Similarly, in the case of three real distinct roots \( D < 0 \) according to Cardano’s method. It follows with Equation (H.26) that
\[
f_{\text{ceos}}(v_{\text{stat},1}) \cdot f_{\text{ceos}}(v_{\text{stat},2}) < 0, \tag{H.33}
\]
Fig. H.4: Cubic function $f_{\cos}(\hat{v}_r)$, restricted to $f_{\cos}(\hat{v}_r) : \mathbb{R} \rightarrow \mathbb{R}$. In the case of one real root it follows $f_{\cos}(v_{\text{stat},1}) \cdot f_{\cos}(v_{\text{stat},2}) > 0$.

Fig. H.5: Cubic function $f_{\cos}(\hat{v}_r)$, restricted to $f_{\cos}(\hat{v}_r) : \mathbb{R} \rightarrow \mathbb{R}$. In the case of three real distinct roots it follows $f_{\cos}(v_{\text{stat},1}) \cdot f_{\cos}(v_{\text{stat},2}) < 0$. 
cf. Figure H.5. From Equations (H.32) and (H.33) it follows that none of the stationary values is a root to $f_{\cos}(\hat{v}_r)$. As a second intermediate result, we obtain, thus, the following: If $D \neq 0$, that is, there are either three distinct real roots or a single real root according to Cardano’s method, we have $f_{\cos}(v_r) = 0 \neq f'_{\cos}(v_r)$, i.e., $v_r$ is a root to $f_{\cos}(\hat{v}_r)$ but not to $f'_{\cos}(\hat{v}_r)$.

Using both intermediate results and from continuity of $f_{\cos}(\hat{v}_r)$ and $f'_{\cos}(\hat{v}_r)$, we conclude that the condition $f'_{\cos}(\hat{v}_r) = 0$ gives the transition between a single real root and three real distinct roots, as suggested in [136] and [46]. Finally, also see [41] for all conceivable shapes of a cubic function.
Constraint Qualifications in Root Discrimination

Disclaimer: This appendix adopts Appendix D entitled “Supplementary data” related to [62]. In this Appendix, Criterion (5.1) and Criterion (5.2) are compared to the root discrimination formulation in [83]. Originally embedded in a phase equilibrium problem, the root discrimination formulation from the literature is considered stand-alone in the present appendix. In particular, it is examined whether the root discrimination formulations satisfy certain CQs. Criterion (5.1) comprises 6 equations in 3 continuous variables. From CQ analysis, it is found that LICQ is satisfied in the case of three distinct real roots, else both LICQ and the Mangasarian Fromovitz constraint qualification (MFCQ) are violated. In contrast, the formulation from the literature comprises 4 equations in 3 variables one of which is binary. This set of equations satisfies LICQ in all root scenarios, except for the (relatively unlikely) case of three real coinciding roots, in which it violates both LICQ and MFCQ. Finally, Criterion (5.2) constitutes 8 equations in 4 variables one of which is binary. This set of equations satisfies LICQ in the case of three distinct real roots and a single real root, while it violates both LICQ and MFCQ in the remaining cases. The discussion on root discrimination has some relevance to but is not to be confused with discussions on phase equilibrium formulations presented in, e.g., [65, 46, 83, 145]. In order to capture a changing number of phases, the latter propose nonsmooth formulations (which violate CQs), while the first suggest Mathematical Programs with Complementarity Constraints (MPCCs) which violate MFCQ and LICQ, see e.g., [18].

I.1 Stand-Alone Interpretation of Kamath et al.

[83] propose a root discrimination formulation and embed it in a phase equilibrium problem formulation in [65]. Arguably the most direct interpretation of their root discrimination formulation as stand-alone is a big-M formulation, see e.g., [76] which reads as follows

\[ h_{11}(x_{ph}, v_{ph,r}) := f_{cos}(x_{ph}, v_{ph,r}) = 0 \]
\[ h_{21}(\theta_i) := \theta_i \cdot (1 - \theta_i) = 0 \]
\[ g_{11}(x_{ph}, v_{ph,r}) := -\left( \frac{\partial f_{cos}}{\partial v} \right)_{x_{ph},v_{ph,r}} \leq 0 \]
\[ g_{21}(x_{ph}, v_{ph,r}, \theta_i) := \left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph},v_{ph,r}} - M_i \cdot \theta_i \leq 0 \]
\[ g_{31}(x_{ph}, v_{ph,r}, \theta_i) := -\left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph},v_{ph,r}} - (1 - \theta_i) \cdot M_i \leq 0, \]

where \( \theta_i \in [0, 1] \) is a real-valued variable, used in further constraints, e.g., related to isopotential and molar flows, and the variables are in the order \( x_{ph}, v_{ph,r}, \theta_i \). In case \( \theta_i = 1 \),
\[ g_{21} \text{ is relaxed, while } g_{31} \text{ is imposed, provided that the value of } M_i \text{ is chosen appropriately.} \]

In contrast, \( \theta_i = 0 \) implies that \( g_{21} \) is imposed, while \( g_{31} \) is relaxed. It should be noted that Equation (I.1b) is a well-known reformulation of \( \hat{\theta}_i \in \{0, 1\} \). This reformulation enables CQ analysis of the mixed-integer formulation, as will be discussed in the next section. Altogether, this results in a set of 5 nonlinear equations in 3 continuous variables.

### 1.2 Proposed Continuous Criterion

The proposed root discrimination formulation (Criterion (5.1)) is presented in Section 5.2.2. Let now \( h_{12} \) denote Equation (5.1a), \( h_{22} \) Equation (5.1b), \( g_{12} \) Equation (5.1c), \( g_{22} \) Equation (5.1d), \( g_{32} \) Equation (5.1e) and \( g_{42} \) Equation (5.1f), where the variables are in the order \( x_{ph}, v_{ph,1}, v_{ph,3} \). Altogether, this results in a set of 6 nonlinear equations in 3 continuous variables.

\[ \begin{align*}
    h_{12}(x_{ph}, v_{ph,1}) &= 0 \quad \text{(I.2a)} \\
    h_{22}(x_{ph}, v_{ph,3}) &= 0 \quad \text{(I.2b)} \\
    h_{21}(\theta_i) &= 0 \quad \text{(I.2c)} \\
    g_{12}(x_{ph}, v_{ph,1}) &\leq 0 \quad \text{(I.2d)} \\
    g_{22}(x_{ph}, v_{ph,3}) &\leq 0 \quad \text{(I.2e)} \\
    g_{13}(x_{ph}, \theta_i) &\leq 0 \quad \text{(I.2f)} \\
    g_{23}(x_{ph}, \theta_i) &\leq 0 \quad \text{(I.2g)} \\
    g_{33}(x_{ph}, v_{ph,1}, \theta_i) &\leq 0 \quad \text{(I.2h)} \\
    g_{43}(x_{ph}, v_{ph,3}, \theta_i) &\leq 0 \quad \text{(I.2i)}
\end{align*} \]

Altogether, this results in a set of 9 nonlinear equations in 4 continuous variables. In case \( \theta_i = 1 \), \( g_{13}, g_{33}, g_{43} \) are relaxed, while \( g_{23} \) is imposed, provided that the value of \( M_i \) is chosen appropriately. It should be noted that for \( \theta_i = 1 \), there might be two distinct real roots which, however, are not guaranteed to be discriminated. On the other hand, for \( \theta_i = 0 \), \( g_{13}, g_{33}, g_{43} \) are imposed, while \( g_{23} \) is relaxed. It should be noted that for \( \theta_i = 0 \), there might be two distinct real roots which will be discriminated. We consider this advantage of Criterion (5.2) over Criterion (5.1) rather minor.

In the following, Equation (I.1), Criterion (5.1) and Equation (I.2) are compared with respect to CQs. LICQ is considered first and if violated, MFCQ is next taken into account. For a definition of LICQ and MFCQ, see e.g., [115]. For CQ analysis, it is required to know the set of active ICs which, in the case of root discrimination formulations, is directly related to the number of roots to the cubic equation. Let \( \mathcal{A} = \{h_i, g_i : g_i = 0, \forall i\} \) denote the set of ECs and active ICs.
I.4 CQs for Stand-Alone Interpretation of Kamath et al.

We will first list the gradients of the ICs and ECs of Equation (I.1), and then analyze CQs for different active sets $A$:

$$\nabla h_{11}(p_{xh},v_{ph},\theta_i) = \left( \begin{array}{c} \frac{\partial f_{ecos}}{\partial x} \\ \frac{\partial f_{ecos}}{\partial v} \end{array} \right)_{x_{ph},v_{ph},\theta_i}, 0 \right)^T (I.3a)$$

$$\nabla h_{21}(p_{xh},v_{ph},\theta_i = 0) = (0, 0, 1)^T (I.3b)$$

$$\nabla h_{21}(p_{xh},v_{ph},\theta_i = 1) = (0, 0, -1)^T (I.3c)$$

$$\nabla g_{11}(p_{xh},v_{ph},\theta_i) = \left( - \begin{array}{c} \frac{\partial^2 f_{ecos}}{\partial x \partial v} \\ - \frac{\partial^2 f_{ecos}}{\partial v^2} \end{array} \right)_{x_{ph},v_{ph},\theta_i}, 0 \right)^T (I.3d)$$

$$\nabla g_{21}(p_{xh},v_{ph},\theta_i) = \left( \begin{array}{c} \frac{\partial^2 f_{ecos}}{\partial x^2 \partial v} \\ 6, -M_i \end{array} \right)_{x_{ph},v_{ph},\theta_i}^T (I.3e)$$

$$\nabla g_{31}(p_{xh},v_{ph},\theta_i) = \left( - \begin{array}{c} \frac{\partial^2 f_{ecos}}{\partial x^2 \partial v} \\ -6, M_i \end{array} \right)_{x_{ph},v_{ph},\theta_i}^T (I.3f)$$

It should be noted that $M_i$ is chosen such that $g_{21}$ is imposed only in case $\theta_i = 0$, while $g_{31}$ is for $\theta_i = 1$. We will exemplify CQ analysis for the first, i.e., $\nabla h_{21}(p_{xh},v_{ph},\theta_i = 0)$ and $g_{21}$; the analysis is equivalent to the case of $\nabla h_{21}(p_{xh},v_{ph},\theta_i = 1)$ and $g_{31}$.

### I.4.1 Three Distinct Real Roots

This case is presumably very likely to occur in, e.g., process simulation, as it generally covers a plane in a $(P,T)$-diagram of potential operating states, see e.g., Figure 5.4. The case of three distinct real roots translates to

$$A_{11} = \{h_{11}, h_{21}\} (I.4)$$

Since $\nabla h_{11}$ and $\nabla h_{21}$ are linearly independent, LICQ holds.

### I.4.2 Single Real Root

This case is presumably very likely to occur in, e.g., process simulation as it generally covers a plane in a $(P,T)$-diagram of potential operating states, see e.g., Figure 5.4. The case of a single real root translates to

$$A_{11} = \{h_{11}, h_{21}\} (I.5)$$

so LICQ holds.

### I.4.3 Two Distinct Real Roots

This case is presumably rather unlikely to occur in, e.g., process simulation, as it represents a line in a $(P,T)$-diagram of potential operating states, see e.g., Figure 5.4. The case of two distinct real roots translates to

$$A_{21} = \{h_{11}, h_{21}, g_{11}\} (I.6)$$
It should be noted that the fact that \( g_{11} \) is active implies
\[
\nabla h_{11}(x_{ph}, v_{ph}, r, \theta) = \left( \frac{\partial f_{\text{cos}}}{\partial x} \right)_{x_{ph}, v_{ph}, r} , 0, 0 \right)^T. 
\]
Assuming that
\[
\det (\nabla h_{11}, \nabla h_{21}, \nabla g_{11}) = \left( \frac{\partial^2 f_{\text{cos}}}{\partial x^2} \right)_{x_{ph}, v_{ph}, r} \cdot \left( \frac{\partial^2 f_{\text{cos}}}{\partial v^2} \right)_{x_{ph}, v_{ph}, r} 
\]
is nonzero (which generally seems a valid assumption), LICQ holds.

### 1.4.4 Three Coinciding Real Roots

This case is presumably rather unlikely to occur in, e.g., process simulation, as it represents a point in a \((P, T)\)-diagram of potential operating states, see e.g., Figure 5.4. The case of three coinciding real roots translates to
\[
\mathcal{A}_{31} = \{h_{11}, h_{21}, g_{11}, g_{21}\}. 
\]
It should be noted that the fact that \( g_{21} \) is active implies
\[
\nabla g_{11}(x_{ph}, v_{ph}, r, \theta) = \left( - \left( \frac{\partial^2 f_{\text{cos}}}{\partial x \partial v} \right), 0, 0 \right)^T. 
\]
Since \( \nabla h_{11} \) and \( \nabla g_{11} \) are linearly dependent, LICQ is violated. Let us now check for MFCQ. \( \nabla h_{11} \) and \( \nabla h_{21} \) are linearly independent which is a necessary criterion for MFCQ. Determine now a direction \( p \in \mathbb{R}^3, p \neq 0 \) such that
\[
\nabla h_{11}^T \cdot p = 0 \\
\nabla h_{21}^T \cdot p = 0, 
\]
e.g., \( p = (0, 1, 0)^T \). Finally, calculate the projections
\[
\nabla g_{11}^T \cdot p = 0 \\
\nabla g_{21}^T \cdot p = 6, 
\]
and hence, MFCQ is violated. As an intermediate result for the stand-alone interpretation of the root discrimination formulation from the literature, the problem is well-posed with respect to CQs in all of the cases, except for the unlikely case of three coinciding roots.

### 1.5 CQs for Proposed Continuous Criterion

We will first list the gradients of the ICs and ECs of Criterion (5.1), and then analyze CQs for different active sets \( \mathcal{A} \):
\[
\nabla h_{12}(x_{ph}, v_{ph,1}, v_{ph,3}) = \left( \frac{\partial f_{\text{cos}}}{\partial x} \right)_{x_{ph}, v_{ph,1}} , \left( \frac{\partial f_{\text{cos}}}{\partial v} \right)_{x_{ph}, v_{ph,1}} , 0 \right)^T
\]
\[ \nabla h_{22}(x_{ph}, u_{ph,1}, u_{ph,3}) = \left( \begin{array}{c} \frac{\partial f_{cos}}{\partial x} \\ \frac{\partial f_{cos}}{\partial v} \\ 0 \end{array} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}}^T \] (I.13b)

\[ \nabla g_{12}(x_{ph}, u_{ph,1}, u_{ph,3}) = \left( \begin{array}{c} -\left( \frac{\partial^2 f_{cos}}{\partial x \partial v} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} \\ -\left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} \end{array} \right)^T \] (I.13c)

\[ \nabla g_{22}(x_{ph}, u_{ph,1}, u_{ph,3}) = \left( \begin{array}{c} -\left( \frac{\partial^2 f_{cos}}{\partial x \partial v} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} \\ -\left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} \end{array} \right)^T \] (I.13d)

\[ \nabla g_{32}(x_{ph}, u_{ph,1}, u_{ph,3}) = \left( \begin{array}{c} -\left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} + D(x_{ph}) \cdot \left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} \\ -6D(x_{ph}) \cdot \left( \frac{\partial^2 f_{cos}}{\partial v^2} \right)_{x_{ph}, u_{ph,1}, u_{ph,3}} \end{array} \right)^T \] (I.13e)

\[ \nabla g_{42}(x_{ph}, u_{ph,1}, u_{ph,3}) = (0, -1, 1)^T. \] (I.13f)

### I.5.1 Three Distinct Real Roots

The case of three distinct real roots translates to

\[ A_{12} = \{h_{12}, h_{22}\}. \] (I.14)

Since \( \nabla h_{12} \) and \( \nabla h_{22} \) are linearly independent, LICQ holds.

### I.5.2 Single Real Root

The case of a single real root translates to

\[ A_{22} = \{h_{12}, h_{22}, g_{42}\}. \] (I.15)

It should be noted that the fact that \( g_{42} \) is active implies

\[ \nabla h_{22}(x_{ph}, u_{ph,1}, u_{ph,3}) = \left( \begin{array}{c} \frac{\partial f_{cos}}{\partial x} \\ \frac{\partial f_{cos}}{\partial v} \\ 0 \end{array} \right)_{x_{ph}, u_{ph,1}, u_{ph,1}}^T. \] (I.16)

Since

\[ \det(\nabla h_{12}, \nabla h_{22}, \nabla g_{42}) = 0, \] (I.17)

LICQ is violated. Let us now check for MFCQ. \( \nabla h_{12} \) and \( \nabla h_{22} \) are linearly independent which is a necessary criterion for MFCQ. Determine now a direction \( p \in \mathbb{R}^3, p \neq 0 \) such that

\[ \nabla h_{12}^T \cdot p = 0 \]
I.6 CQs for Proposed Mixed-Integer Criterion

\[ \nabla h_{22}^T \cdot p = 0, \quad (I.18) \]

e.g., \( p = \begin{pmatrix} -\left( \frac{\partial f_{\text{cos}}}{\partial v} \right) |_{x_{ph,v_{ph,1}},v_{ph,1}} \cdot \left( \frac{\partial f_{\text{cos}}}{\partial \theta} \right) |_{x_{ph,v_{ph,1}}} \cdot \left( \frac{\partial f_{\text{cos}}}{\partial x} \right) |_{x_{ph,v_{ph,1}}} \end{pmatrix}^T \). Finally, calculate the projection

\[ \nabla g_{42}^T \cdot p = 0. \quad (I.19) \]

Hence, MFCQ is violated.

I.5.3 Two Distinct Real Roots

Criterion (5.1) is not guaranteed to discriminate between the roots in this case. Consider first the case of coinciding root variables \( v_{ph,1} = v_{ph,3} \), resulting in either

\[ A_{32} = \{ h_{12}, h_{22}, g_{12}, g_{42} \} \quad (I.20) \]

or

\[ A_{42} = \{ h_{12}, h_{22}, g_{22}, g_{42} \}. \quad (I.21) \]

Since \( A_{22} \subseteq A_{32} \) and \( A_{22} \subseteq A_{42} \), LICQ and MFCQ are violated. The case of distinct root variables \( v_{ph,1} \neq v_{ph,3} \) resulting in either

\[ A_{52} = \{ h_{12}, h_{22}, g_{12} \} \quad (I.22) \]

or

\[ A_{62} = \{ h_{12}, h_{22}, g_{22} \} \quad (I.23) \]

is not considered further since it cannot be guaranteed, although it is the desirable case.

I.5.4 Three Coinciding Real Roots

The case of three coinciding real roots translates to

\[ A_{72} = \{ h_{12}, h_{22}, g_{12}, g_{22}, g_{32}, g_{42} \}. \quad (I.24) \]

Since \( A_{22} \subseteq A_{72} \), LICQ and MFCQ are violated. As an intermediate result for Criterion (5.1), the problem is well-posed with respect to CQs only in the likely case of three distinct real roots. In all of the other cases, both MFCQ and LICQ are violated and thus, at least in theory, this might cause difficulties in applying optimization algorithms to a problem formulation with this root discrimination formulation imposed as a set of constraints.

I.6 CQs for Proposed Mixed-Integer Criterion

We will first list the gradients of the ICs and ECs of Equation (I.2), and then analyze CQs for different active sets \( \mathcal{A} \):

\[ \nabla h_{12}(x_{ph,v_{ph,1}},v_{ph,3},\theta_1) = \begin{pmatrix} \left( \frac{\partial f_{\text{cos}}}{\partial x} \right) |_{x_{ph,v_{ph,1}}} \cdot \left( \frac{\partial f_{\text{cos}}}{\partial \theta} \right) |_{x_{ph,v_{ph,1}}} \cdot \left( \frac{\partial f_{\text{cos}}}{\partial v} \right) |_{x_{ph,v_{ph,1}}} \end{pmatrix}^T \quad (I.25a) \]
\[ \nabla h_{22}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( \begin{array}{c} \left( \frac{\partial f_{\text{cos}}}{\partial x} \right)_{x_{ph},v_{ph,1}} \, 0, \left( \frac{\partial f_{\text{cos}}}{\partial v} \right)_{x_{ph},v_{ph,1}} \end{array} \right)^T \]  
(I.25b)

\[ \nabla h_{21}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i = 0) = (0, 0, 0, 1)^T \]  
(I.25c)

\[ \nabla h_{21}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i = 1) = (0, 0, 0, -1)^T \]  
(I.25d)

\[ \nabla g_{12}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( -\left( \frac{\partial^2 f_{\text{cos}}}{\partial^2 x} \right)_{x_{ph},v_{ph,1}}, -\left( \frac{\partial^2 f_{\text{cos}}}{\partial^2 v} \right)_{x_{ph},v_{ph,1}} \right)^T \]  
(I.25e)

\[ \nabla g_{22}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( -\left( \frac{\partial^2 f_{\text{cos}}}{\partial^2 x} \right)_{x_{ph},v_{ph,1}}, 0, \left( \frac{\partial^2 f_{\text{cos}}}{\partial^2 v} \right)_{x_{ph},v_{ph,1}} \right)^T \]  
(I.25f)

\[ \nabla g_{13}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( -\left( \frac{\partial D}{\partial x} \right)_{x_{ph}}, 0, 0, -M_1 \right)^T \]  
(I.25g)

\[ \nabla g_{23}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( -\left( \frac{\partial D}{\partial x} \right)_{x_{ph}}, 0, 0, M_2 \right)^T \]  
(I.25h)

\[ \nabla g_{33}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( -\left( \frac{\partial^3 f_{\text{cos}}}{\partial x \partial^2 v} \right)_{x_{ph},v_{ph,1}}, -6, 0, -M_3 \right)^T \]  
(I.25i)

\[ \nabla g_{43}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( \frac{\partial^3 f_{\text{cos}}}{\partial x \partial^2 v} \right)_{x_{ph},v_{ph,1}}, 0, 6, -M_4 \right)^T \]  
(I.25j)

### I.6.1 Three Distinct Real Roots

The case of three distinct real roots translates to \( \theta_i = 0 \) and

\[ A_{13} = \{ h_{12}, h_{22}, h_{21} \}, \]  
(I.26)

and since these are linearly independent, LICQ holds.

### I.6.2 Single Real Root

The case of a single real root translates to \( \theta_i = 1 \) and

\[ A_{23} = A_{13}. \]  
(I.27)

It should be noted that the single-real-root case implies

\[ \nabla h_{22}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( \frac{\partial f_{\text{cos}}}{\partial x} \right)_{x_{ph},v_{ph,1}}, 0, \left( \frac{\partial f_{\text{cos}}}{\partial v} \right)_{x_{ph},v_{ph,1}} \right)^T. \]  
(I.28)

Since \( \nabla h_{12}, \nabla h_{22} \) and \( \nabla h_{21} \) are linearly independent, LICQ holds.
I.6 CQs for Proposed Mixed-Integer Criterion

I.6.3 Two Distinct Real Roots

Criterion (5.2) is not guaranteed to discriminate between the roots in this case if \( \theta_i = 1 \). We will consider the case of coinciding root variables \( v_{ph,1} = v_{ph,3} \) since the other case cannot be guaranteed, yet it is the desirable one, for \( \theta_i = 1 \). For \( \theta_i = 0 \), the criterion does discriminate the roots. Let us first discuss the scenario of \( \theta_i = 0 \), i.e., \( v_{ph,1} \neq v_{ph,3} \). Then, either

\[
\mathcal{A}_{43} = \{ h_{12}, h_{22}, h_{21}, g_{12}, g_{13} \},
\]

where

\[
\nabla h_{12}(x_{ph}, v_{ph,1}, v_{ph,3}; \theta_i) = \left( \frac{\partial f_{\text{cos}}}{\partial x} \right)_{x_{ph}, v_{ph,1}}^T, 0, 0, 0
\]

or

\[
\mathcal{A}_{43} = \{ h_{12}, h_{22}, h_{21}, g_{22}, g_{13} \},
\]

where

\[
\nabla h_{22}(x_{ph}, v_{ph,1}, v_{ph,3}; \theta_i) = \left( \frac{\partial f_{\text{cos}}}{\partial x} \right)_{x_{ph}, v_{ph,3}}^T, 0, 0, 0
\]

Since

\[
\det (\nabla h_{12}, \nabla h_{22}, \nabla h_{21}, \nabla g_{13}) = 0
\]

for both \( \mathcal{A}_{33} \) and \( \mathcal{A}_{43} \), LICQ is violated. Let us now check for MFCQ. \( \nabla h_{12}, \nabla h_{22} \) and \( \nabla h_{21} \) are linearly independent for both \( \mathcal{A}_{33} \) and \( \mathcal{A}_{43} \) which is a necessary criterion for MFCQ. Determine now directions \( p_1, p_2 \in \mathbb{R}^4 \), \( p_1 \neq 0, p_2 \neq 0 \), one for each case, such that

\[
\nabla h_{12}^T \cdot p_i = 0, \quad i = 1, 2
\]

\[
\nabla h_{22}^T \cdot p_i = 0,
\]

\[
\nabla h_{21}^T \cdot p_i = 0,
\]

e.g., \( p_1 = (0, 1, 0, 0)^T \) and \( p_2 = (0, 0, 1, 0)^T \). Finally, calculate the projections

\[
\nabla g_{12}^T \cdot p_1 = - \left( \frac{\partial^2 f_{\text{cos}}}{\partial v^2} \right)_{x_{ph}, v_{ph,1}}
\]

\[
\nabla g_{13}^T \cdot p_1 = 0,
\]

and

\[
\nabla g_{22}^T \cdot p_2 = - \left( \frac{\partial^2 f_{\text{cos}}}{\partial v^2} \right)_{x_{ph}, v_{ph,3}}
\]

\[
\nabla g_{13}^T \cdot p_2 = 0,
\]

respectively. Hence, MFCQ is violated for both \( \mathcal{A}_{33} \) and \( \mathcal{A}_{43} \). Let us now discuss the scenario of \( \theta_i = 1 \), i.e., \( v_{ph,1} = v_{ph,3} \). Then, either

\[
\mathcal{A}_{53} = \{ h_{12}, h_{22}, h_{21}, g_{12}, g_{23} \},
\]
I Constraint Qualifications in Root Discrimination

or

\[ A_{63} = \{ h_{12}, h_{22}, h_{21}, g_{22}, g_{23} \}. \]  

(I.38)

Since

\[
\nabla h_{12}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) = \left( \begin{array}{c} \frac{\partial f_{cos}}{\partial x} \\ 0, 0, 0 \end{array} \right)_{x_{ph},v_{ph,1}}^T
\]

\[ = \nabla h_{22}(x_{ph}, v_{ph,1}, v_{ph,3}, \theta_i) \]  

(I.39)

in either case, both LICQ and MFCQ are violated.

I.6.4 Three Coinciding Real Roots

The case of three coinciding real roots translates to either \( \theta_i = 0 \) and

\[ A_{73} = \{ h_{12}, h_{22}, h_{21}, g_{12}, g_{22}, g_{13}, g_{33}, g_{43} \}. \]  

(I.40)

or to \( \theta_i = 1 \) and

\[ A_{83} = \{ h_{12}, h_{22}, h_{21}, g_{12}, g_{22}, g_{23}, g_{33}, g_{43} \}. \]  

(I.41)

Since \( A_{33} \subset A_{73} \) and \( A_{53} \subset A_{83} \), LICQ and MFCQ are violated in either case. As an intermediate result for Criterion (5.2), the problem is well-posed with respect to CQs only in the likely cases of three distinct real roots and a single real root. In the remaining (rather unlikely) cases, both MFCQ and LICQ are violated.
J Theoretical and Numerical Results for CEOS

Disclaimer: This appendix adopts an abridged and slightly modified version of Appendix A entitled “Supplementary data” related to [60]. We would like to add that the adopted Sections J.4.1 and J.4.2 are, in turn, mainly adoptions of the direct proof of Baker’s criterion and the conclusions on the convexity of the Gibbs free energy from [106]. The extensions of [106] in this thesis consist of notational issues, the addition of Lemma 2 as an alternative to [106, Lemma 12], and Equation J.37. This appendix is a modified version of [60, Appendix] in that the author cites only the linear mixing rule Equation (J.7), yet not the quadratic one from the literature as the latter leads to thermodynamic inconsistency.

J.1 Problem Formulations

As opposed to $\Delta G^E$ models, CEOS models are cast in the space of both mole fraction and molar volume, calling for criteria for both phase and mechanical stability. In the following, the problem formulation (5.43) proposed in the main part will be discussed in more detail for a specific LLP, in order to illustrate how mechanical stability is encoded. In our opinion, regression problems should consider mechanical stability in some form or other, e.g., root discrimination criteria, in order to prevent different root types from being assigned to the same phase. This will be the case if there exists more than one real root to a CEOS, and the respective regression solver detects that mixing those roots and phase types allows for a decrease in the objective function $f(\cdot)$.

J.1.1 “Trilevel” Problem Statement

For root discrimination by means of a Gibbs free energy minimization, the parameter estimation problem results in a trilevel program, e.g.,

\[
\begin{align*}
\min_{x_u, v_1^u, v_3^u, q^u} & \quad f^u(x_u, v_1^u, v_3^u, q^u) \\
\text{s.t.} & \quad h^u(x_u, v_1^u, v_3^u, q^u) = 0 \quad (J.1a) \\
& \quad \Delta G(x_u, v_1^u, v_3^u, q^u) - \Delta G(x_u, v_1^u, v_3^u, q^u) \geq 0 \quad (J.1b) \\
& \quad \left(x_u, v_1^u, v_3^u, q^u\right) \in \arg\min_{x_l, v_1^l, v_3^l, q^l} \left(\Delta G(x_l, v_1^l, v_3^l, q^l) - \Delta G(x_l, v_1^l, v_3^l, q^l)\right) \quad (J.1c) \\
& \quad \text{s.t.} g^{l,1,lp}(x_u, x_l, q^u) \geq 0 \quad (J.1d) \\
& \quad v_1^l \in \arg\max_{v_2, v_3^l} \Delta G(x_l, v_1^l, v_2, q^u) \quad (J.1e)
\end{align*}
\]
J Theoretical and Numerical Results for CEOS

\[ f_{\text{ceos}}(x^{l,lp}, v_1^{l,lp}, q_u^l) = 0 \quad (J.1g) \]

\[ f_{\text{ceos},v}(x^{l,lp}, v_1^{l,lp}, q_u^l) \geq 0 \quad (J.1h) \]

\[ v_3^{l,lp} \in \arg\min_{v_3^{l,lp}} \Delta G \left( x^{l,lp}, v_3^{l,lp}, q_u^l \right) \quad (J.1i) \]

\[ s.t. \ f_{\text{ceos}}(x^{l,lp}, v_3^{l,lp}, q_u^l) = 0 \quad (J.1j) \]

... \[ x^{l,lp} \in X^{l,lp}, v_r^{l,lp} \in V^{l,lp}, x^{n,lp} \in X^{n,lp}, \]

\[ v_r^{u,lp} \in V^{u,lp}, x^u \in X^u, v_r^u \in V^u, q_u^l \in Q^u, \]

where we consider only a certain LLP \( llp \) and omit, for the sake of brevity, the variables \( x^{n,lp}, v_1^{n,lp}, v_3^{n,lp} \) in Equation (J.1a). According to [83] Equation (J.1h) excludes the intermediate root; for further discussion, cf. [62]. Without this constraint, \( v_1^{l,lp} \) would be the intermediate root in the lower-level maximization problem (J.1f) [112]. This is the reason why, on the contrary, Equation (J.1h) is not required for Problem (J.1i). If a desired root \( v_r^{l,lp} \) does not exist, Problems (J.1f) and (J.1i) remain feasible, and Equation (J.1c) is trivially satisfied. Since for this specific trilevel program, to the author’s best knowledge, no algorithms yet exist in the open literature, reformulations to a bilevel program are required. For instance, the lowest level could be cast as a black box with a simple solver to select the desired Gibbs free energy from among up to three distinct values, making Problem (J.1) a bilevel program. Alternatively, reformulations given by, e.g., Problem (J.2), respectively, are conceivable which are more amenable to global optimization and which is, thus, pursued in the present work.

### J.1.2 Bilevel Problem Restatement

In order to make Problem (J.1) amenable to state-of-the-art algorithms, we reformulate it to a BLP according to

\[ \min_{x^u, v_1^u, v_3^u} f^u(x^u, v_1^u, v_3^u, q_u^l) \quad (J.1a) \]

\[ \text{s.t. } h^u(x^u, v_1^u, v_3^u, q_u^l) = 0 \quad (J.1b) \]

\[ \Delta G \left( x^{u,lp}, v_1^{u,lp}, q_u^l \right) - \Delta G \left( x^{n,lp}, v_3^{n,lp}, q_u^l \right) \geq 0 \]

\[ \left( x^{u,lp}, v_1^{u,lp}, v_3^{u,lp} \right) \in \arg\min_{x^{l,lp}, v_1^{l,lp}, v_3^{l,lp}} \left( \Delta G \left( x^{l,lp}, v_1^{l,lp}, q_u^l \right) - \Delta G \left( x^{l,lp}, v_3^{l,lp}, q_u^l \right) \right) \quad (J.2a) \]

\[ \text{s.t. } g^{l,lp} \left( x^u, x^{l,lp} \right) \geq 0 \quad (J.2b) \]

\[ f_{\text{ceos}}(x^{l,lp}, v_1^{l,lp}, q_u^l) = 0 \quad (J.2c) \]

\[ f_{\text{ceos}}(x^{l,lp}, v_3^{l,lp}, q_u^l) = 0 \quad (J.2d) \]

\[ g^{EQ,lp} \left( x^{l,lp}, v_1^{l,lp}, v_3^{l,lp}, q_u^l \right) \geq 0 \quad (J.2e) \]

...
Equation (J.2f) shall constitute a root discrimination criterion based on ICs which, on the one hand, casts \( v_{l,1} \), \( v_{l,1} \) the undesired roots, and on the other, \( v_{u,3} \), \( v_{l,3} \) the desired ones. \( v_{u,1} \) and \( v_{l,1} \) are then communicated to Equation (J.2a) to check for mechanical stability of the desired root.

There is a further argument in favor of root discrimination criteria. Considering (i) that a rigorous root discrimination criterion is a minimization of \( \Delta G \) with respect to \( v_{ph,r} \) at \( T, P, x_i \), \( const. \), and (ii) that the LLP by itself is a minimization of \( \Delta G \) with respect to \( x_i \), it might seem straightforward to formulate the minimization of \( \Delta G \) with respect to both variables. While this may hold for an objective which is simply the Gibbs free energy, it is not necessarily correct for, e.g., differences of the Gibbs free energy. Without Equation (J.2f), \( v_{u,1} \) and \( v_{l,1} \) would represent the stable, and \( v_{u,3} \) and \( v_{l,3} \) the unstable roots due to Equation (J.2b) [112]. As a result, Equation (J.2a) would be violated.

### J.2 Thermodynamic Fundamentals

The following well-known equations are used in this work and given in, e.g., [162]. Let

\[
\left( \frac{\partial \phi}{\partial x_i} \right)_{\hat{x},v_{ph,r}} \text{ denote the first-order derivative of } (\cdot) \text{ with respect to mole fraction } x_i \text{ at } T, P, q = \text{ const., evaluated at } \dot{x}, \hat{v}_{ph,r}, \hat{q}, \hat{T}, \hat{P}, \text{ and let } \phi_i \text{ be the fugacity coefficient.}
\]

According to Euler’s equation

\[
\Delta G_{ph} (T, P, x_{ph}, v_{ph,r}) = \sum_{i=1}^{N-1} \Delta \mu_i (T, P, x_{ph}, v_{ph,r}) \cdot x_i + \Delta \mu_{N,ph} (T, P, x_{ph}, v_{ph,r}) \cdot \left( 1 - \sum_{i=1}^{N-1} x_i \right). \tag{J.3}
\]

Exploiting the Gibbs-Duhem equation, cf. e.g., [162], relation the first-order derivative of Equation (J.3) reads

\[
\left( \frac{\partial \Delta G_{ph}}{\partial x_i} \right)_{x_{ph},v_{ph,r}} = \Delta \mu_i (T, P, x_{ph}, v_{ph,r}) - \Delta \mu_{N,ph} (T, P, x_{ph}, v_{ph,r}). \tag{J.4}
\]

noting that \( \Delta \mu_i \) is the key variable in Equations (J.3) and (J.4). Relative to the reference state “ideal mixture of ideal gases” which often is appropriate for the \( \phi - \phi \) approach, \( \Delta \mu_i \) is given by

\[
\Delta \mu_i (T, P, x_{ph}, v_{ph,r}) = RT \cdot \ln (x_i \phi_i \phi_i (T, P, x_{ph}, v_{ph,r})). \tag{J.5}
\]

Equation (J.5) may be plugged into Equations (J.3) and (J.4) to yield expressions for the reduced Gibbs free energy and its first derivative.

### J.2.1 CEOS Models

In the following, let us omit the subscript \( ph \) to indicate the phase, and let \( T_{c,i} \) and \( P_{c,i} \) denote the critical temperature and pressure of species \( i \), respectively, and \( \omega_i \) its
accentric factor. Let further \( k_{a,ij} \) be the binary interaction parameter to be regressed, \( Z_r \) the compressibility factor and \( \partial a_i, \partial b_i \) the terms related to the partial differentiation of the residual Helmholtz free energy with respect to mole fraction \( x_i \), dependent on the mixing rule. For instance, quadratic mixing rules, cf. e.g., [9, 175]

\[
A_{\text{mix}} = \sum_i \sum_j x_i x_j A_{ij} \quad (J.6)
\]

\[
B_{\text{mix}} = \sum_i x_i B_i \quad (J.7)
\]
yield

\[
\partial a_i = 2 \sum_j A_{ij} x_j \quad (J.8)
\]

\[
\partial b_i = B_i \quad (J.9)
\]

with the combining rules given by

\[
A_{ij} = (1 - k_{a,ij}) \sqrt{A_i A_j} \quad (J.10)
\]

\[
B_{ij} = \frac{B_i + B_j}{2}, \quad (J.11)
\]

noting that \( A_{ii} = A_i, B_{ii} = B_i, A_{ij} = A_{ji}, B_{ij} = B_{ji} \). For the prominent SRK model, we follow [72] who propose the reformulations

\[
w_r = v_r - B_{\text{mix}} > 0 \quad (J.12)
\]

\[
0 = v_r^3 - v_r^2 + (A_{\text{mix}} - B_{\text{mix}} - (B_{\text{mix}})^2) \cdot v_r - A_{\text{mix}} B_{\text{mix}} \quad (J.13)
\]

\[
\ln \varphi_i = \frac{\partial b_i}{B_{\text{mix}}} (v_r - 1) - \ln w_r + \frac{A_{\text{mix}}}{B_{\text{mix}}} \left( \frac{\partial b_i}{B_{\text{mix}}} - \frac{\partial a_i}{A_{\text{mix}}} \right) \ln \left( 1 + \frac{B_{\text{mix}}}{v_r} \right), \quad (J.14)
\]

where the intermediate variable \( w_r \) serves, among others, the purpose of ensuring physically sensible roots, and

\[
A_i = 0.42747 \frac{PT_{c,i}^2}{P_{c,i} T} \left( 1 + \left(0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \right) \cdot \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right)^2 \quad (J.15)
\]

\[
B_i = 0.08664 \frac{PT_{c,i}^2}{P_{c,i} T} \quad (J.16)
\]

Similarly, for the well-known PR model, cf. [72],

\[
0 = v_r^3 - (1 - B_{\text{mix}}) \cdot v_r^2 + (A_{\text{mix}} - 2B_{\text{mix}} - 3(B_{\text{mix}})^2) \cdot v_r - A_{\text{mix}} B_{\text{mix}} \quad (J.17)
\]

\[
\ln \varphi_i = \frac{\partial b_i}{B_{\text{mix}}} (v_r - 1) - \ln w_r + \frac{A_{\text{mix}}}{2\sqrt{2}B_{\text{mix}}} \left( \frac{\partial b_i}{B_{\text{mix}}} - \frac{\partial a_i}{A_{\text{mix}}} \right) \ln \left( \frac{v_r + (1 + \sqrt{2})B_{\text{mix}}}{v_r + (2 - \sqrt{2})B_{\text{mix}}} \right), \quad (J.18)
\]
where

\[
A_i = 0.45724 \frac{PT_{ci}^2}{P_{c,i}T^2} \left( 1 + (0.37464 + 1.54226\omega_i - 0.26992\omega_i^2) \right) \left( 1 - \sqrt{\frac{T}{T_{c,i}}} \right)^2 \quad (J.19)
\]

\[
B_i = 0.07780 \frac{PT_{ci}}{P_{c,i}T} \quad (J.20)
\]

### J.3 Measurement and Regressed Data

**Table J.1:** Isothermal VLE measurement data in [140] for mole fraction \(x\) of \(\text{C}_5\text{H}_{12}\) for \(\text{C}_5\text{H}_{12}/\text{H}_2\text{S}\) at 344.23 K.

<table>
<thead>
<tr>
<th>(P) (kN m(^{-2}))</th>
<th>(x) liquid (mol mol(^{-1}))</th>
<th>(x) vapor (mol mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4826.3</td>
<td>0.1</td>
<td>0.019</td>
</tr>
<tr>
<td>4136.9</td>
<td>0.2313</td>
<td>0.0447</td>
</tr>
<tr>
<td>3447.4</td>
<td>0.3628</td>
<td>0.0723</td>
</tr>
<tr>
<td>2757.9</td>
<td>0.5005</td>
<td>0.116</td>
</tr>
<tr>
<td>2068.4</td>
<td>0.6374</td>
<td>0.1721</td>
</tr>
<tr>
<td>1379.0</td>
<td>0.7782</td>
<td>0.2645</td>
</tr>
<tr>
<td>689.48</td>
<td>0.9201</td>
<td>0.4876</td>
</tr>
</tbody>
</table>

**Table J.2:** Model predictions by BOARPET [109] for mole fraction \(x\) of \(\text{C}_5\text{H}_{12}\) and compressibility factor \(Z\) for VLE of \(\text{C}_5\text{H}_{12}/\text{H}_2\text{S}\), and comparison with RGibbs’ [7] flash results. The PR model is fitted to isothermal VLE data from [140] as given in Table J.1. Pressure and temperature are set to the measurements for the regression.

<table>
<thead>
<tr>
<th>RGibbs (simulation)</th>
<th>BOARPET (regression)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x) liquid mol mol(^{-1})</td>
<td>(x) vapor mol mol(^{-1})</td>
</tr>
<tr>
<td>0.09935</td>
<td>0.029385</td>
</tr>
<tr>
<td>0.23177</td>
<td>0.054354</td>
</tr>
<tr>
<td>0.36936</td>
<td>0.077232</td>
</tr>
<tr>
<td>0.50739</td>
<td>0.10415</td>
</tr>
<tr>
<td>0.64449</td>
<td>0.14359</td>
</tr>
<tr>
<td>0.78135</td>
<td>0.21747</td>
</tr>
<tr>
<td>0.91916</td>
<td>0.43106</td>
</tr>
</tbody>
</table>
Table J.3: Model predictions by BOARPET [109] for mole fraction $x$ of C$_5$H$_{12}$ and compressibility factor $Z$ for VLE of C$_5$H$_{12}$/H$_2$S, and comparison with RGibbs’ [7] flash results. The SRK model is fitted to isothermal VLE data from [140] as given in Table J.1. Pressure and temperature are set to the measurements for the regression.

<table>
<thead>
<tr>
<th>R.Gibbs (simulation)</th>
<th>BOARPET (regression)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$ liquid (mol mol$^{-1}$)</td>
<td>$x$ vapor (mol mol$^{-1}$)</td>
</tr>
<tr>
<td>0.10017</td>
<td>0.028362</td>
</tr>
<tr>
<td>0.23056</td>
<td>0.052599</td>
</tr>
<tr>
<td>0.36722</td>
<td>0.075355</td>
</tr>
<tr>
<td>0.50507</td>
<td>0.10247</td>
</tr>
<tr>
<td>0.64256</td>
<td>0.14238</td>
</tr>
<tr>
<td>0.7802</td>
<td>0.21726</td>
</tr>
<tr>
<td>0.91908</td>
<td>0.43376</td>
</tr>
</tbody>
</table>

J.4 Tangent Plane Criterion

State-of-the-art is a tangent plane stability criterion of Baker et al. and follow-ups [12, 154, 81, 80] for the Gibbs free energy with respect to mole fraction, $\Delta G(x)$. The criterion is both sufficient and necessary for phase stability. In the case of CEOS models, a second state variable is present, the molar volume $v_r$, which is subject to mechanical stability. In this section, we formally show that the satisfaction of phase stability remains unaffected by the presence of an additional variable, and the applicability of Baker’s criterion is warranted. (It should be noted that this is not sufficient for mechanical stability which requires additional criteria.)

The effect of a second state variable on the applicability of the tangent plane criterion for $\Delta G(x)$ seems undiscussed in the open literature. [12, 154, 81, 80, 106] give proof of a tangent plane criterion for the Gibbs free energy with respect to mole fraction at $T, P = \text{const.}$ [82] mention a tangent criterion for $\Delta A$ for pure species. [66] derive such a criterion for mixtures with respect to molar density and molar volume, from first-order KKT conditions for the minimization of $\Delta A$. [112] prove the tangent criterion for $\Delta A$ with respect to density and volume. [128] present a tangent criterion for $\Delta A$ with respect to mole fraction and volume using a dual problem formulation based on [106].

In contrast, a tangent criterion for $\Delta G$ is, at least, in the form it is postulated, not directly applicable to any thermodynamic model that considers additional state variables, such as the molar volume $v_r$, or related variables. In this case, the first step is to formulate

$$\Delta G^* (x) = \min_{v_r} \Delta G (x, v_r). \quad \text(J.21)$$

Subsequently, [106, Theorem 5] is applicable to $\Delta G^* (x)$. Similarly, [12, Example 1] postulate that the tangent plane criterion is indirectly applicable to CEOS models, namely after satisfying mechanical stability: “ . . . there is more than one possible Gibbs energy at each composition because there are three real compressibility solutions for the equation of state. In calculating a Gibbs energy curve, where there are multiple real compressibility solutions of the equation of state, only the solution giving the lowest Gibbs energy should be considered”. 

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In this section, we present a tangent plane criterion that allows \( v_r \) as a state variable and guarantees phase stability. Hence, the criterion is formally and directly applicable to CEOS models. In particular, said tangent plane does not exhibit the partial derivative of \( \Delta G(x, v_r) \) with respect to \( v_r \). The proof mainly adopts the direct proof of Baker’s criterion given in [106, Appendix] and in most parts, our extension concerns only notation. The implications of the tangent plane criterion for convexity of \( \Delta G(x, v_r, q) \) are outlined. We conclude with a remark on the requirement of differentiability of the surface of the Gibbs free energy for [12].

### J.4.1 Proof of Tangent Plane Criterion

As a complement to Theorem 1, we use the following mathematical interpretation of thermodynamic stability in terms of phase equilibrium for our proof in this section.

**Theorem 4** At a given temperature \( T^0 \), pressure \( P^0 \) and overall number of moles \( n_i^0 \) for the species \( i = 1, \ldots, n \), a state described by a collection of phases with compositions \( x_{ph} \), with total mole numbers in each phase \( n_{t,ph} \) such that \( \sum_{ph} n_{t,ph} x_{i,ph} = n_i^0, \forall i = 1, \ldots, N \) and with molar volume \( v_{r,ph} \) of each phase, is stable for \( r \in \{1,3\} \) if and only if among all possible states, for a nonreactive system, it has the lowest Gibbs free energy, i.e.,

\[
\Delta G_{ph} = \sum_{j \in J} n_{t,ph} \Delta G(x_{ph}, v_{r,ph}) \leq \sum_{k \in K} n_{t,k} \Delta G(x_k, v_{r,k}) = \Delta G_K,
\]

\[\forall (K, n_{t,k}, x_k) : \left\{ \sum_{k \in K} n_{t,k} x_{i,k} = n_i^0, \forall i = 1, \ldots, N; \ P(x_k, v_{r,k}) - P^0 = 0 \right\}, \tag{J.22}\]

where \( \Delta G \) and \( \Delta G \) are the molar and the total Gibbs free energy, respectively.

The following Lemma 2 is based on [106, Lemma 12], in that we consider a limiting value problem. We use L’Hôpital’s rule for it is straightforward and no further geometric theorems are needed. In contrast, in [106] the theorem of intersecting lines is applied instead of L’Hôpital’s rule.

**Lemma 2** Let \( Z \subset \mathbb{R} \) be an interval and \( z^0 \) be an interior point of this interval, \( z^0 \in \text{int}(Z) \). Consider \( f : Z \to \mathbb{R} \), differentiable on \( \text{int}(Z) \). Denote the derivative \( f' : \text{int}(Z) \to \mathbb{R} \). Consider also the tangent \( t^0 \) at the point \( z^0 \) given by

\[ t^0(z) = f(z^0) + f'(z^0)(z - z^0). \tag{J.23} \]

If there exists a point \( z^l \in Z \) such that \( z^l < z^0 \) and \( t^0(z^l) > f(z^l) \), then there exists \( h > 0 \), such that all points \( z^{ll} \in (z^0, z^0 + h) \) satisfy

\[ f(z^l) + \frac{f(z^{ll}) - f(z^l)}{z^{ll} - z^l} (z^0 - z^l) < f(z^0). \tag{J.24} \]

**Proof** Consider the secant \( s^{l,0} \) through points \((z^0, f(z^0))\) and \((z^l, f(z^l))\) given by

\[ s^{l,0}(z) = f(z^l) + \frac{f(z^0) - f(z^l)}{z^0 - z^l} (z - z^l), \tag{J.25} \]
and points $z^h = z^0 + h$. From the limiting value problem applying L’Hôpital’s rule, we have

$$\lim_{z^h \to z^0} \left( \frac{s^{I.0}(z^h) - f(z^h)}{z^h - z^0} \right) = \lim_{z^h \to z^0} \left( \frac{(s^{I.0})'(z^h) - f'(z^h)}{\partial(z^h-z^0)} \right) = \frac{f(z^0) - f(z^I)}{z^0 - z^I} - f'(z^0) \right)$$

(J.26)

$$= \frac{1}{(z^0 - z^I)} \left( f(z^0) - f(z^I) \right) - f'(z^0) \right)$$

(J.27)

by the definition of $t^0(z)$

$$= \frac{1}{(z^0 - z^I)} \left( f(z^0) - f(z^I) \right) - \frac{t^0(z^I) - f(z^0)}{z^I - z^0} \left( z^I - z^0 \right)$$

(J.28)

$$= \frac{t^0(z^I) - f(z^I)}{z^I - z^0}.$$ \hspace{0.5cm} (J.29)

Since $t^0(z^I) > f(z^I), z^0 > z^I$, by assumption

$$\lim_{z^h \to z^0} \left( \frac{s^{I.0}(z^h) - f(z^h)}{z^h - z^0} \right) > 0.$$ \hspace{0.5cm} (J.30)

It follows for sufficiently small $h$ that $s^{I.0}(z^h) > f(z^h)$. Now take such a point $z^h$ and denote it $z^{II}$. Consider the secant $s^{I,II}$ through points $(z^I, f(z^I))$ and $(z^{II}, f(z^{II}))$ given by

$$s^{I,II}(z) = f(z^I) + \frac{f(z^{II}) - f(z^I)}{z^{II} - z^I} (z - z^I).$$ \hspace{0.5cm} (J.31)

Since both $s^{I.0}$ and $s^{I,II}$ are affine, $s^{I.0}(z^I) = s^{I,II}(z^I)$, and $s^{I.0}(z^{II}) > f(z^{II}) = s^{I,II}(z^{II})$, we have $s^{I.0}(z) > s^{I,II}(z) \ \forall z \in (z^I, z^{II})$. In particular, for $z = z^0$, we have

$$f(z^I) + \frac{f(z^{II}) - f(z^I)}{z^{II} - z^I} (z^0 - z^I) = s^{I,II}(z^0) < s^{I.0}(z^0) = f(z^0).$$ \hspace{0.5cm} (J.32)

It should be noted that since $z^0 \in \text{int}(Z)$ for sufficiently small $h$, we also have $z^h \in Z$. □

Baker’s criterion [12] to ensure the fulfilment of phase stability can be extended to the variable space $(x_{ph}, v_r)$ without affecting the applicability of its original version, as follows:

**Theorem 5** Consider a system at a given temperature $T^0$ and pressure $P^0$ and an overall mole number $n_i^0 > 0$ for the species $i = 1, \ldots, N$. Denote $n_{i,0} = \sum_{i=1}^{N} n_i^0$. Consider a state described by a collection of phases $ph = 1, \ldots, Ph$, composition $\mathbf{x} \in \text{int}(X)$ where

$$X = \left\{ x \in [0,1]^{N-1} : \sum_{i=1}^{N-1} x_i < 1 \right\},$$

molar volume of phase $ph$, $v_{r,ph} \in \text{int}(V(\mathbf{x}))$, where cubic equality is satisfied and covolume $b_{ceos}(\mathbf{x})$ according to the equation of state is considered,

$$V : X \to \mathbb{R},$$

$$V(\mathbf{x}) = \left\{ v_r \in (b_{ceos}(\mathbf{x}), \infty) : P(\mathbf{x}, v_r) - P^0 = 0, \ r \in \{1, 3\} \right\},$$

$$\sum_{i=1}^{N-1} x_i < 1.$$
with nonzero total mole number in each phase \( n_{t,ph} > 0 \) such that
\[
\sum_{ph} n_{t,ph} x_{i,ph} = n_i^0, \quad \forall i = 1, \ldots, N - 1.
\] (J.33)

Consider finally the associated tangent at \((x^*_p, v^*_r)\) for some \( ph \) and \( r \in \{1, 3\}\),
\[
\Theta_1(x) = \Delta G(x^*_p, v^*_r) + \sum_{i=1}^{N-1} G_x(x^*_p, v^*_r, ph) \cdot (x_i - x^*_{i,ph}).
\] (J.34)

The phases of the state are stable if and only if for all \( x \in \text{int}(X) \) and \( v_r \in \text{int}(V(x)) \)
\[
\Theta_1(x) \leq \Delta G(x, v_r) \quad \text{ (J.35)}
\]
\[
\Theta_1(x) = \Delta G(x^*_p, v^*_r, ph) + \sum_{i=1}^{N-1} G_x(x^*_p, v^*_r, ph) \cdot (x_i - x^*_{i,ph}), \quad \forall ph.
\] (J.36)

**Proof** We will directly come to the core of the proof and show that \( \Theta_1(x) \) is tangent to \( \Delta G(x, v_r) \) if \( x \in \text{int}(X) \) and \( v_r \in \text{int}(V(x)) \), in particular, as long as cubic equality is met \( P(x, v_r) - P^0 = 0 \). We use a formulation introduced in [112].

From Legendre transformation, we have \( \Delta G = \Delta A + Pv_r \), where \( \Delta A \) is the molar Helmholtz free energy. In particular, by assumption, \( \Delta G = \Delta A + P^0v_r \). In the following, we will abbreviate the partial differentials for all \( x \in \text{int}(X) \) and \( v_r \in \text{int}(V(x)) \), as follows:
\[
\left(\frac{\partial \Delta G}{\partial x_i}\right)_{P,T,x_{k\neq i}} = G_{x_i},
\]
\[
\left(\frac{\partial \Delta G}{\partial v_r}\right)_{T,x_i} = G_{v_r},
\]
\[
\left(\frac{\partial \Delta A}{\partial x_i}\right)_{T,x_{k\neq i}} = A_{x_i},
\]
\[
\left(\frac{\partial \Delta A}{\partial v_r}\right)_{T,x_i} = A_{v_r}.
\]

For the partial differential, it follows
\[
G_{v_r} = A_{v_r} + P^0
\]
\[
= -P(x, v_r) + P^0
\]
by cubic equality
\[
= 0.
\] (J.37)

Consider the tangent \( \Theta_2(x, v_r) \) to \( \Delta G(x, v_r) \) at \((x^*_p, v^*_r, ph)\) for some \( ph \) and \( r \in \{1, 3\}\)
\[
\Theta_2(x, v_r) = \Delta G(x^*_p, v^*_r, ph) + \sum_{i=1}^{N-1} G_x(x^*_p, v^*_r, ph) \cdot (x_i - x^*_{i,ph})
\]
\[
+ G_{v_r}(x^*_p, v^*_r, ph) \cdot (v_r - v^*_{r,ph}),
\] (J.38)
where \( \mathbf{x}, \mathbf{x}_{ph}^* \in \text{int}(X) \) and \( v_r, v_{r,ph}^* \in \text{int}(V(\mathbf{x})) \). With Equation (J.37), it follows that \( \Theta_2(\mathbf{x}, v_r) = \Theta_1(\mathbf{x}) \) for all \( v_r \in \text{int}(V(\mathbf{x})) \). In the remainder of this proof, our extension of Baker’s criterion is mainly an adoption of the Appendix “Mathematical Results and Proofs” in [106].

In the following, we will first show the necessity and then the sufficiency for Theorem 5.

1. Necessity of Equation (J.35): If the phases of the state \((\mathbf{x}, v_r)\) are stable, we have \( \Theta_1(\mathbf{x}) \leq \Delta G(\mathbf{x}, v_r), \forall \mathbf{x} \in \text{int}(X), \; v_r \in \text{int}(V(\mathbf{x})) \). This part proceeds by contraposition and uses [106, Lemma 12]. Suppose that for some \( \bar{\mathbf{x}} \in \text{int}(X) \) and \( \bar{v}_r \in \text{int}(V(\mathbf{x})) \), we have

\[
\Theta_1(\bar{\mathbf{x}}) > \Delta G(\bar{\mathbf{x}}, \bar{v}_r).
\]

(J.39)

According to [106, Lemma 12] we can find a secant through \((\bar{\mathbf{x}}, \bar{v}_r)\) and \((\bar{\mathbf{x}}, \tilde{v}_r)\) such that for a feed \((\mathbf{x}_{ph}^*, v_{r,ph}^*)\) and \( \kappa \in (0, 1) \),

\[
\mathbf{x}_{ph}^* = \kappa \bar{\mathbf{x}} + (1 - \kappa) \tilde{\mathbf{x}} \tag{J.40}
\]

\[
\Delta G(\mathbf{x}_{ph}^*, v_{r,ph}^*) > \kappa \Delta G(\bar{\mathbf{x}}, \bar{v}_r) + (1 - \kappa) \Delta G(\tilde{\mathbf{x}}, \tilde{v}_r). \tag{J.41}
\]

Since \( \mathbf{x}_{ph}^* \in \text{int}(X) \) and the point \( \tilde{\mathbf{x}} \) can be found arbitrarily close to \( \mathbf{x}_{ph}^* \), we also have \( \tilde{\mathbf{x}} \in \text{int}(X) \). We can therefore, reduce \( \Delta G \) by replacing phase \( ph \) with, at least, two phases of compositions \( \tilde{\mathbf{x}} \) and \( \tilde{\mathbf{x}} \). According to Theorem 4 the state is not stable.

2. Necessity of Equation (J.36): If the phases of the state are stable, the tangents taken at any phase coincide for the same phase split. Since isopotential is a necessary criterion for phase stability, e.g., [162], we will show that the tangents taken at any phase coincide provided isopotential holds.

From thermodynamics it is well-known, e.g., [162] that

\[
G_{x_i}(\mathbf{x}_{ph}, v_{r,ph}) = \Delta \mu_{i,ph}(\mathbf{x}_{ph}, v_{r,ph}) - \Delta \mu_{N,ph}(\mathbf{x}_{ph}, v_{r,ph}),
\]

\[
\forall i = 1, \ldots, N - 1, \; \forall ph, \; r = 1, 3. \tag{J.42}
\]

Together with isopotential according to

\[
\Delta \mu_{i,ph}(\mathbf{x}_{ph}, v_{r,ph}) = \Delta \mu_{i,ph}^*(\mathbf{x}_{ph}^*, v_{r,ph}^*),
\]

\[
\forall i = 1, \ldots, N, \; \forall ph, \; r = 1, 3, \tag{J.43}
\]

it follows that the slopes of the tangents are equal

\[
G_{x_i}(\mathbf{x}_{ph}, v_{r,ph}) = G_{x_i}(\mathbf{x}_{ph}^*, v_{r,ph}^*). \tag{J.44}
\]

Similarly, from thermodynamics it is known, e.g., [162] that

\[
\Delta \mu_{N,ph}(\mathbf{x}_{ph}, v_{r,ph}) = \Delta G(\mathbf{x}_{ph}, v_{r,ph}) - \sum_{i=1}^{N-1} x_{i,ph} G_{x_i}(\mathbf{x}_{ph}, v_{r,ph}). \tag{J.45}
\]

Together with isopotential according to

\[
\Delta \mu_{N,ph}(\mathbf{x}_{ph}, v_{r,ph}) = \Delta \mu_{N,ph}^*(\mathbf{x}_{ph}^*, v_{r,ph}^*), \; \forall ph, \; r = 1, 3, \tag{J.46}
\]
this yields

\[ \Delta G(x_{ph}, v_{r,ph}) - \sum_{i=1}^{N-1} x_{i,ph} G_x(x_{ph}, v_{r,ph}) = \Delta G(x_{ph}^*, v_{r,ph}^*) - \sum_{i=1}^{N-1} x_{i,ph}^* G_x(x_{ph}^*, v_{r,ph}^*). \] (J.47)

Adding \( \sum_{i=1}^{N-1} G_x(x_{ph}, v_{r,ph}) \cdot x_i \) and \( \sum_{i=1}^{N-1} G_x(x_{ph}^*, v_{r,ph}^*) \cdot x_i \) to LHS and RHS, respectively, we obtain

\[ \Delta G(x_{ph}, v_{r,ph}) + \sum_{i=1}^{N-1} G_x(x_{ph}, v_{r,ph}) \cdot (x_i - x_{i,ph}) = \Delta G(x_{ph}^*, v_{r,ph}^*) + \sum_{i=1}^{N-1} G_x(x_{ph}^*, v_{r,ph}^*) \cdot (x_i - x_{i,ph}^*) = \Theta_1(x). \] (J.48)

3. Sufficiency

For \( r \in \{1, 3\} \) consider a collection of phases \( ph = I, \ldots, Ph \), for which the total Gibbs free energy is

\[ \Delta G_{Ph} = \sum_{ph} n_{t,ph} \Delta G(x_{ph}, v_{r,ph}) \]

by definition of the tangent

\[ = \sum_{ph} n_{t,ph} \Theta_1(x_{ph}) \]

\[ = n_t^0 \Theta_1(x^0). \] (J.49)

On the other hand, consider any other collection of phases \( k = I, \ldots, K \) and \( r \in \{1, 3\} \), for which \( \sum_{k \in K} n_{t,k} x_{i,k} = n_t^0, \forall i = 1, \ldots, N \) and \( P(x_k, v_{r,k}) - P^0 = 0 \). We have

\[ \Delta G_K = \sum_{k \in K} n_{t,k} \Delta G(x_k, v_{r,k}) \]

by assumption

\[ \geq \sum_{k \in K} n_{t,k} \Theta_1(x_k) \]

\[ = n_t^0 \Theta_1(x^0) \]

\[ = \Delta G_{Ph}, \ \forall (K, n_{t,k}, x_k). \] (J.50)

By Theorem 4 the phases indexed with \( ph \) of the state are stable for \( r \in \{1, 3\} \).

\[ \square \]

**J.4.2 Implications for Convexity**

Assume the existence of the Hessian \( H_G(x_{ph}, v_{r,ph}) \) of \( \Delta G(x_{ph}, v_{r,ph}) \) at a state \( (x_{ph}, v_{r,ph}) \). Consider a tangent \( \Theta_1(x) \) with a point of tangency \( (x_{ph}, v_{r,ph}) \). A direct consequence of
Theorem 5 is that if \( \Theta_1(x) \leq \Delta G(x, v_r) \) for all \( x \in \text{int}(X) \) and some \( r \in \{1, 3\} \), the state satisfies the necessary condition for phase stability, i.e., the Hessian is positive semi-definite at the point of tangency \((x_{ph}, v_{r,ph})\) [162, Equation (7-15)]. In particular, the Gibbs free energy surface is locally convex, i.e., at \((x_{ph}, v_{r,ph})\) the necessary condition for phase stability is satisfied

\[
\left( \frac{\partial^2 \Delta G}{\partial x_i^2} \right)_{P,T,x_{\text{ext},ph}} \geq 0, \forall ph, \forall i = 1, \ldots, N. \tag{J.51}
\]

Local convexity at \((x_{ph}, v_{r,ph})\) implies that

\[
\Theta_1(x) = \Delta G(x_{ph}, v_{r,ph}) + \sum_{i=1}^{N-1} G_{x_i}(x_{ph}, v_{r,ph}) \cdot (x_i - x_{i,ph}) \\
\leq \Delta G(x, v_r), \\
\forall x \in \text{int}(X), \forall i = 1, \ldots, N, \\
\forall x_{ph} \in \text{int}(\hat{X}), v_{r,ph} \in \text{int}(\hat{V}(x_{ph})), p h = 1, \ldots, P h, \\
i = 1, \ldots, N, \quad r = 1, 3,
\]

where

\[
\hat{X} = \left\{ x_{ph} \in [x_{lo}, x_{up}]^{N-1} : \sum_{i=1}^{N-1} x_{i,ph} < 1, \quad x_{lo}, x_{up} \in [0, 1] \right\},
\]

and

\[
\hat{V}(x_{ph}) = \left\{ v \in (b_{cos}(x_{ph}), \infty) : P(x_{ph}, v_{r,ph}) - P^0 = 0 \right\},
\]

is a sufficient condition for convexity of \( \Delta G(x_{ph}, v_{r,ph}) \) on \( \hat{X} \) [106].

**J.4.3 Remarks on Differentiability**

For a binary mixture, i.e., \( N = 2 \), there are cases conceivable in which there exists \( x_{i,ph} \in (0, 1) \) at which

\[
\Delta G(x_{ph}) = \min\{ \Delta \bar{G}_{ph}(x_{ph}, v_{1,ph}), \Delta \bar{G}_{ph}(x_{ph}, v_{2,ph}), \Delta \bar{G}_{ph}(x_{ph}, v_{3,ph}) \} \tag{J.53}
\]

is nondifferentiable in \( x_{ph} \), also see [73]. In the following, we will argue that the tangent criterion [12] which relies on differentiability, at least, at the points of tangency \( x_{ph}^* \), is indeed applicable.

According to the fundamental theorem of algebra applied to cubic functions, the set

\[
G(x_{ph}) = \{ \Delta \bar{G}(x_{ph}) \Delta \bar{G}(x_{ph}) \}
\]

is guaranteed to be nonempty for any \( x_{ph} \in (0, 1)^{N-1} \). Now, the regressed parameters \( \mathbf{q} \) are constrained to isopotential (J.43), and differentiability of \( \Delta G \) at \( x_{ph} = x_{ph}^* \) is a well-known necessary condition for isopotential. Therefore, there exist unique gradients at \( x_{ph}^* \), the points of tangency, and Baker’s criterion [12] remains applicable.
Bibliography

[1] Data Preparation Package (DPP), 2014 DECHEMA, Gesellschaft für Chemische Technik und Biotechnologie e.V.


