Gibbs Phase Rule and the Duhem Theorem: An Introduction

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Abstract– This work presents a rigorous thermodynamic analysis of the Gibbs Phase Rule (GPR) and the Duhem theorem, emphasizing their complementary roles in defining and constraining phase equilibrium. The GPR quantifies the degrees of freedom (DOF) in multicomponent systems, while the Duhem theorem establishes functional dependencies among intensive variables in closed systems. A structured methodological framework is proposed to integrate both principles into computational thermodynamics, enabling systematic validation of equilibrium models. Recent advances in CALPHAD, activity coefficient models, and high-dimensional thermodynamics are critically evaluated. Applications in CO_2 capture, electrolyte systems, and advanced materials demonstrate the practical relevance of the combined framework. Limitations related to non-equilibrium behavior and high-dimensional constraints are discussed, and future research directions are identified.

Keywords-- Degree of Freedom; Duhem's Theorem; Gibbs Phase Rule; Intensive and extensive variables; Phase equilibrium.

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I. Introduction

Phase equilibrium constitutes a vital pillar of classical and applied thermodynamics, providing the theoretical basis for understanding how multiple phases coexist under defined thermodynamic conditions. At equilibrium, a system exhibits no net macroscopic transfer of mass or energy, and its state can be described through a set of intensive variables such as pressure (P), temperature (T), and chemical potentials (μ). This unified framework is crucial for interpreting phase behavior in systems ranging from simple pure substances to highly complex multicomponent mixtures encountered in chemical engineering, materials science, and geochemical processes [1], [2].

The quantitative description of phase equilibrium is usually governed by the GPR, which establishes a relationship between the number of components, phases, and DOF in a system. This rule has been widely adopted for the analysis of phase diagrams and the design of equilibrium-based processes. However, recent developments in thermodynamic modeling have confirmed that classical formulations of the GPR may require generalization when applied to high-dimensional systems or systems influenced by additional intensive variables such as interfacial effects, electric fields, or mechanical constraints [2], [3]. These advances highlight the need to revisit classical thermodynamic principles within the context of modern applications.

Despite their shared foundation in equilibrium thermodynamics, the GPR and the Duhem theorem address fundamentally different aspects of the problem. The GPR defines the structural DOF of a system, indicating how many variables can vary independently without violating equilibrium. In contrast, the Duhem theorem provides a closure condition, specifying how many variables are required to uniquely define the system once constraints are imposed. This distinction is especially important in multi-component and high-dimensional systems, where improper interpretation of these principles may lead to inconsistencies in both theoretical analysis and computational implementation [3], [4], [5].

In recent years, the increasing complexity of thermodynamic systems, traditionally in areas such as electrolyte solutions, carbon capture technologies, and advanced materials, has exposed limitations in classical equilibrium frameworks [6]. Modern approaches, including CALPHAD-based methods and activity coefficient models such as NRTL and UNIFAC, rely on concurrent application of GPR and Gibbs–Duhem relation to ensure thermodynamic consistency and predictive reliability. These frameworks have demonstrated strong performance in modeling non-ideal systems; however, their accuracy depends critically on consistent integration of thermodynamic constraints and validation against experimental data [7].

Notwithstanding these advances, the literature reveals a lack of unified methodologies that systematically integrate the GPR and Duhem theorem into a coherent analytical and computational framework. Most existing approaches treat these principles independently, which can lead to fragmented interpretations and reduced robustness in complex systems, particularly those involving additional variables or high-dimensional phase spaces [3].

Accordingly, the primary objective of this work is to develop a structured and unified interpretation of the GPR and the Duhem theorem, emphasizing their complementary roles in phase equilibrium analysis. This study introduces a reproducible thermodynamic evaluation framework that integrates DOF analysis, constraint mapping, and consistency verification.

By bridging classical theory with modern computational practices, the work aims to enhance the robustness, applicability, and interpretability of thermodynamic models used in both academic research and industrial applications. Furthermore, it identifies key limitations in current approaches and outlines future directions for extending equilibrium thermodynamics to high-dimensional and non-equilibrium systems.

II. METHODOLOGY

This review proposes a structured thermodynamic analysis framework designed to systematically integrate the GPR and the Duhem theorem within theoretical and computational frameworks. Unlike conventional narrative reviews, this methodology emphasizes reproducibility, traceability, and quantitative consistency by combining analytical derivations, computational validation, and literature-based comparison.

The methodological approach is grounded in a critical documentary analysis, supported by a targeted review of peer-reviewed literature published between 2020 and 2026. Databases including Scopus, Web of Science, and ScienceDirect were used to identify studies addressing phase equilibrium, computational thermodynamics, and generalized formulations of thermodynamic constraints. The emphasis was placed on works involving CALPHAD modeling and activity coefficient methods, given their central role in modern thermodynamic applications [8].

The first stage of the methodology involves the formal identification of thermodynamic frameworks, focusing on the derivation and assumptions underlying both the GPR and the Duhem theorem. Systems were classified according to the number of components (N), number of phases (π), and system constraints (open vs closed). This classification is essential because the applicability of each thermodynamic principle depends directly on these characteristics. In particular, the Duhem theorem requires a closed system with fixed composition, whereas the GPR applies more generally across equilibrium systems.

The theoretical formulation of phase equilibrium was revisited through the equality of chemical potential across phases:

$$\mu_i^{(1)} = \mu_i^{(2)} = \cdots = \mu_i^{(\pi)} \qquad (1)$$

This condition generates N (π−1) independent constraints, which reduces the number of independent variables in the system. The identification of these constraints forms the basis for subsequent DOF analysis and provides a rigorous link between thermodynamic theory and computational execution. The second stage focuses on DOF mapping, using the classical GPR:

$$\boldsymbol{F = 2 + N - \pi} \qquad (2)$$

This equation was systematically applied across representative systems, including single-component, multi-component, and high-dimensional systems. Particular attention was given to cases where additional intensive variables (e.g., interfacial energy or external fields) modify the classical formulation, requiring generalized forms of the phase rule. Recent studies have shown that such extensions are necessary for accurately describing complex materials systems and high-dimensional phase spaces.

To aid the GPR analysis, the Gibbs–Duhem relation was employed as a consistency criterion:

$$\sum_{i=1}^{N} x_i \cdot d \cdot \ln(\gamma_i) = 0 \qquad (3)$$

This equation ensures that activity coefficients remain thermodynamically consistent across compositions. In this work, it is used not only as a validation tool but also as a diagnostic criterion to identify inconsistencies in experimental datasets and computational models.

The third stage involves computational thermodynamic models, particularly CALPHAD and activity-coefficient approaches such as NRTL and UNIFAC. These methods determine equilibrium through thermodynamic-potential minimization or phase-equilibrium equations [9], [10]. Python-based implementations can provide a transparent environment for reproducing such calculations [11].

A critical aspect of the methodology is the integration of theoretical constraints into computational workflows. The equality of chemical potentials and Gibbs–Duhem consistency were enforced numerically to ensure that model predictions satisfy fundamental thermodynamic principles. This integration is essential for achieving reliable predictions in multicomponent systems, particularly those exhibiting strong non-ideal behavior [4].

Model validation was performed through comparison with experimental data reported in the literature, focusing on phase equilibria in electrolyte systems, alloys, and reactive mixtures. Discrepancies between predicted and experimental data were analyzed in terms of thermodynamic inconsistency, parameter estimation errors, and limitations of the underlying models. This step provides a critical bridge between theory and real-world application [3].

A key contribution of this methodology lies in the explicit tracking of thermodynamic constraints across all stages of analysis. Unlike traditional approaches that treat GPR and Duhem independently, this work integrates both principles into a unified workflow that simultaneously accounts for structural DOF and functional dependencies among variables. This dual perspective enhances both interpretability and predictive capability [12].

From a comparative standpoint, existing methodologies often emphasize either computational modeling or theoretical derivation but rarely combine both in a systematic manner. For example, CALPHAD-based studies typically focus on parameter optimization without explicitly analyzing DOF constraints, while theoretical works may not address computational implementation. This gap limits the ability to ensure thermodynamic consistency across complex systems [8].

Furthermore, current research often lacks standardized validation protocols for assessing thermodynamic consistency in multicomponent systems [2]. While the Gibbs–Duhem relation is widely recognized, it is not consistently applied as a

validation tool in computational studies. This work addresses this limitation by including consistency checks as a pillar of the methodology [13].

Another limitation identified in the literature is the insufficient treatment of high-dimensional thermodynamic systems, where additional variables beyond temperature and pressure play a significant role. Recent advances in computational thermodynamics suggest that classical frameworks must be extended to incorporate these variables, yet practical methodologies for doing so remain underdeveloped [6], [14], [15], [16].

Finally, the proposed methodology outlines several future research directions, including the extension of the framework to non-equilibrium systems, coupling with kinetic models, and integration with machine learning approaches for thermodynamic prediction. These directions are aligned with recent trends in computational thermodynamics, where hybrid approaches are increasingly used to overcome the limitations of purely equilibrium-based models.

To evaluate the proposed framework, an illustrative thermodynamic simulation of the binary CO_2–methanol system was performed at 5066.25 kPa. The working calculation used the supplied NRTL parameters for liquid-phase non-ideality together with the vapor-pressure correlations and reference equilibrium data listed in Tables I–III. The simulation was implemented in Python using a Google Colaboratory notebook [17]. Because the present calculation is intended as a consistency and phase-behavior exercise, rather than as a validated high-pressure correlation, quantitative extrapolation outside the tabulated conditions would require additional verification with an appropriate fugacity/equation-of-state treatment.

TABLE I
NRTL MODEL PARAMETERS

Parameters	
α	0.30
τ_{12}	0.854
τ_{21}	1.243

TABLE II
ANTOINE-EQUATION PARAMETERS USED IN THE WORKING MODEL

Antoine-equation parameters			
	A	B	C
CO_2	15.3284	1821.12	239.11
Methanol	16.5785	3638.27	239.50

TABLE III
REFERENCE EQUILIBRIUM DATA USED FOR COMPARISON

Parameters		
X	Y	T (°C)
0.0	0.0	140.2
0.12	0.45	122.5
0.25	0.72	105.1
0.38	0.84	88.00
0.51	0.91	71.20
0.65	0.95	53.40
0.72	0.97	42.10

Using these inputs, three graphical outputs were generated: (i) an isobaric T–x–y representation used to compare the calculated equilibrium envelope with the reference points, (ii) the liquid and vapor phase fractions for an overall CO_2 composition $z_1 = 0.35$, and (iii) an internal Gibbs–Duhem consistency residual for the NRTL activity-coefficient calculation.

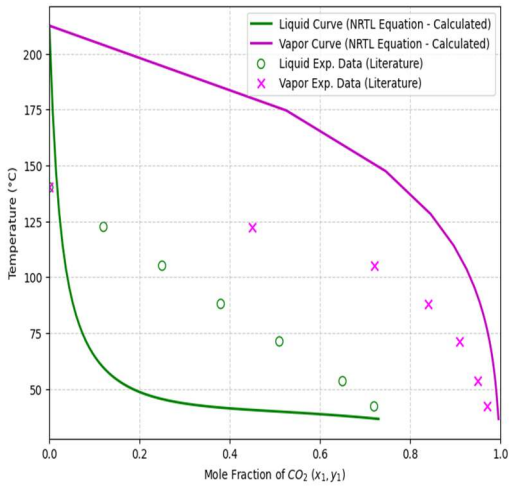


Fig. 1. Isobaric T–x–y representation for the CO_2–methanol working model at 5066.25 kPa, including the reference equilibrium points used for comparison.

The T–x–y diagram describes the calculated liquid–vapor equilibrium envelope at constant pressure. The bubble and dew curves delimit the calculated two-phase region, while the reference points provide a direct comparison between the working model and the data used in the simulation. The comparison is interpreted qualitatively because the present parameter set has not been independently re-fitted or validated over a broader high-pressure range.

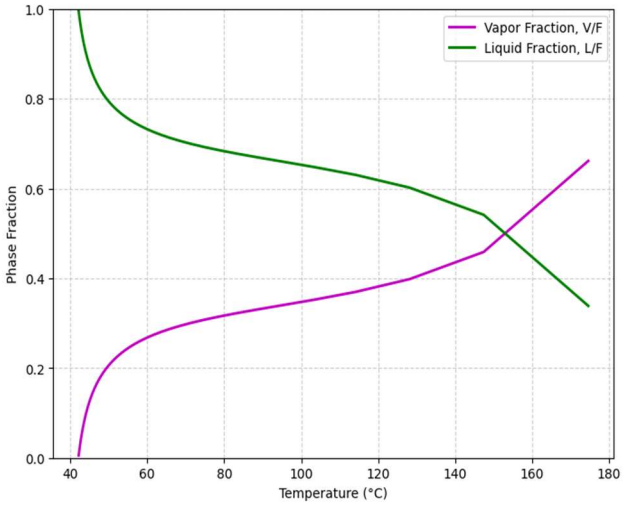


Fig. 2. Calculated liquid (L/F) and vapor (V/F) phase fractions for $z_1 = 0.35$ at 5066.25 kPa.

For a fixed overall composition of $z_1 = 0.35$, the equilibrium phase compositions were combined with the lever rule to calculate the liquid (L/F) and vapor (V/F) fractions as temperature changes through the two-phase region. This calculation represents material distribution between coexisting phases and complements the degree-of-freedom analysis; it should not be interpreted as a direct verification of the Duhem theorem.

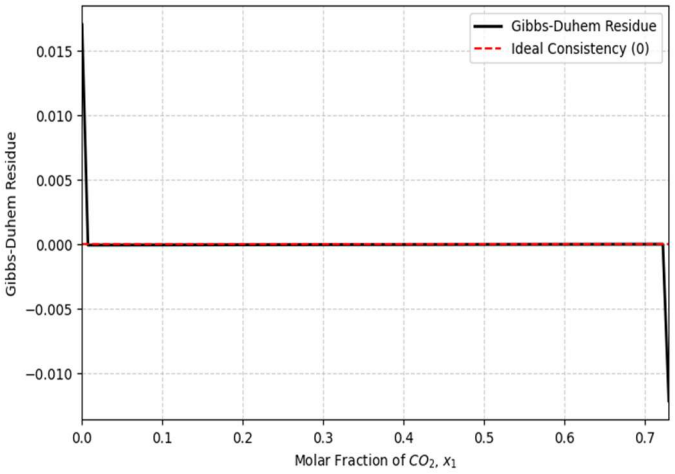


Fig. 3. Gibbs–Duhem consistency residual calculated from the NRTL activity coefficients.

Thermodynamic consistency of the activity-coefficient calculation was assessed using the Gibbs–Duhem relation at fixed temperature and pressure. For a binary mixture, the fixed-condition consistency check was evaluated using (3).

A residual close to zero indicates mutual consistency of the composition dependence of the two calculated activity coefficients. This test is conceptually distinct from the isobaric T–x–y path, along which temperature changes with composition; therefore, the Gibbs–Duhem residual is interpreted as a separate fixed-condition consistency check.

III. DISCUSSION AND RESULTS

A. *Fundamentals of Phase Equilibrium*

Thermodynamically, a system is in phase equilibrium when no macroscopic driving force exists that promotes a net transfer of mass or energy between coexisting phases. This condition is satisfied when thermal, mechanical, and chemical equilibrium are concurrently achieved, ensuring that temperature, pressure, and chemical potential remain uniform through the system. This definition is consistent with modern formulations of thermodynamic stability in multicomponent systems and provides the conceptual basis for equilibrium modeling [2].

Thermal equilibrium requires a common temperature, mechanical equilibrium a common pressure, and chemical equilibrium equality of the chemical potential of each component across coexisting phases, as expressed in (1). These conditions prevent net heat, mechanical, and mass transfer at equilibrium [8].

In multicomponent systems, enforcing these conditions analytically becomes increasingly complex due to the coupling between variables. As a result, modern approaches rely on numerical minimization of thermodynamic potentials to simultaneously satisfy equilibrium constraints. This computational perspective has become essential in accurately describing systems with strong non-ideal interactions and multiple phases [7].

The relevance of this framework is evident in advanced applications such as reactive systems, electrolyte solutions, and multiphase separations. In these cases, deviations from ideality require incorporating activity coefficients and excess Gibbs energy models, further increasing model complexity. Consequently, equilibrium analysis must be supported by rigorous thermodynamic theory and robust computational methods [18].

Recent studies emphasize that equilibrium should not be interpreted solely as a static condition but as the endpoint of a dynamic process governed by minimization of free energy. This perspective is particularly important in systems where metastable states exist due to kinetic barriers. Understanding this distinction is critical for interpreting experimental observations and validating thermodynamic models [19].

B. *Thermodynamic Variables and Systems Classification*

The classification of thermodynamic variables into intensive and extensive properties is essential for defining the state of a system and determining its DOF. Extensive variables, such as volume and mass, depend on system size, whereas intensive variables, including temperature, pressure, and chemical potential, remain invariant. This distinction underpins the formulation of equilibrium relationships and phase rules [1].

The transition from single-component to multicomponent systems introduces composition variables that increase system dimensionality. Whereas a single-component equilibrium can often be represented primarily in temperature–pressure space, multicomponent systems require additional composition coordinates and therefore more careful degree-of-freedom accounting.

The expansion of thermodynamic space presents other limitations that must be satisfied to maintain equilibrium. These constraints arise from conservation laws and equilibrium conditions, leading to complex interdependencies among variables. Thus, incorrect classification or omission of variables can lead to significant errors in phase equilibrium predictions [3].

In systems with strong non-ideal interactions or additional external fields, assumptions regarding variable independence may need to be re-examined. Generalized formulations of the phase rule have therefore been proposed for systems with additional non-compositional state variables [3].

C. *Thermodynamic Potentials and Stability Criteria*

At constant temperature and pressure, stability is governed by minimization of the Gibbs free energy. A stable equilibrium corresponds to a minimum of the appropriate thermodynamic potential; metastable states may persist when kinetic barriers prevent access to the global minimum [2].

These conditions ensure both equilibrium and local stability, distinguishing stable states from unstable or metastable configurations [2].

Stable equilibrium corresponds to the global minimum of the applicable thermodynamic potential, whereas local minima can represent metastable states. This distinction is especially relevant in crystallization and phase-separation processes, where kinetic barriers may delay attainment of the global equilibrium state.

Modern computational tools such as CALPHAD and molecular simulations depend on this minimization principle to determine phase stability. These approaches solve high-dimensional problems to identify equilibrium states, integrating experimental data with theoretical models. Their success relies on the accuracy of thermodynamic databases and interaction parameters [10].

The importance of stability criteria extends to emerging materials systems, where multiple metastable states may coexist. In such systems, thermodynamic analysis must be complemented by kinetic considerations to fully describe observed behavior. This highlights the need for integrated thermodynamic–kinetic frameworks [19].

D. Phase Diagrams and Multidimensional Equilibrium Surfaces

Phase diagrams provide a graphical representation of equilibrium conditions and phase stability. In binary systems, these diagrams are typically expressed as temperature–composition or pressure–composition plots. However, for multicomponent systems, equilibrium exists in high-dimensional spaces that cannot be directly visualized [3].

The transition from binary diagrams to multicomponent phase spaces reflects increasing thermodynamic dimensionality. Binary systems can often be visualized directly, whereas multicomponent equilibria generally require projections, sections, or computational representations.

Phase diagrams encode critical information about phase coexistence, stability regions, and transformation pathways. Their interpretation requires a clear understanding of thermodynamic constraints and DOF. Inaccurate interpretation can lead to incorrect predictions of system behavior, particularly in industrial applications.

Recent advances in computational thermodynamics have enabled the construction of high-dimensional phase diagrams using numerical methods. These approaches integrate experimental data with thermodynamic models to generate predictive phase maps. Such developments are essential for designing advanced materials and optimizing chemical processes [3].

The integration of machine learning with thermodynamic modeling represents a promising direction for improving phase diagram prediction. These methods can identify patterns in complex datasets and enhance predictive accuracy. However, ensuring thermodynamic consistency remains a critical challenge [1].

E. Gibbs Phase Rule and Degrees of Freedom

The Gibbs Phase Rule used in the methodology (2) relates the number of components, phases, and degrees of freedom at equilibrium.

The rule defines the number of independent intensive variables required to specify an equilibrium state under the assumptions of the classical formulation [3].

As the number of coexisting phases increases, the available degrees of freedom decrease because additional equilibrium constraints are introduced. For a single-component system with three coexisting phases, F = 0, corresponding to invariant conditions.

The practical application of the GPR extends to chemical engineering, materials science, and geochemistry, where it guides interpretation of phase behavior and experimental design [3].

Recent studies have proposed extensions of the GPR to account for additional variables such as electric fields and interfacial effects. These generalized formulations expand their applicability to modern systems but require careful validation. This highlights the evolving relevance of classical thermodynamic principles [20].

F. Limitations and Extensions of the GPR

Classical thermodynamic frameworks, including the GPR and Duhem theorem, are derived under strict equilibrium assumptions. They do not account for kinetic limitations, transport phenomena, or transient states. As a result, real systems often exhibit deviations from theoretical predictions [21].

Metastability represents a major limitation in equilibrium analysis, as systems may remain trapped in local energy minimum. This behavior is common in crystallization, polymer systems, and phase separation processes. In such cases, thermodynamic predictions must be complemented with kinetic models [19].

Non-ideal behavior introduces additional complexity, requiring the use of activity coefficient models. While Gibbs–Duhem equation ensures internal consistency, it does not define the useful form of these models. Consequently, empirical or semi-empirical approaches are often necessary [3]. Table IV summarizes key limitations of the classical frameworks considered here.

TABLE IV
GPR AND DUHEM-THEOREM LIMITATIONS COMPARISON

Aspect	GPR	Duhem Theorem
Equilibrium assumption	Strict	Strict
Kinetic effects	Not included	Not included
Non-ideal behavior	Requires constitutive models	Not model-specific
Additional fields	Requires generalized form	Constraints must be reformulated
Dimensional extension	Generalizable	Constraint-dependent

Recent research emphasizes the need for generalized thermodynamic frameworks that incorporate additional variables and non-equilibrium effects. These developments are

essential for accurately describing modern materials systems [20].

G. Duhem Theorem and Thermodynamic Constraints

The Duhem theorem states that, for a closed equilibrium system of fixed total composition, not all intensive variables can be varied independently. This general dependence should be distinguished from the Gibbs–Duhem relation, which supplies a differential consistency condition among partial molar properties and, for activity-coefficient models at fixed temperature and pressure, leads to Eq. (3) [12], [13].

Accordingly, the Gibbs–Duhem relation is used here as the numerical consistency criterion introduced in the methodology rather than as a second, independent phase rule.

Satisfaction of (3) indicates that the activity coefficients are mutually consistent with the thermodynamic constraint at the specified fixed conditions.

This distinction is important because fixing two intensive variables in a closed equilibrium system constrains the remaining state variables through the applicable thermodynamic relations; it does not imply that every two-variable choice is universally independent.

Recent studies emphasize that enforcing Gibbs–Duhem consistency is critical in advanced modeling approaches such as phase-field simulations and CALPHAD-based frameworks [10]. Failure to satisfy this constraint leads to inconsistencies in predicted phase equilibria and deviations from experimental observations [12].

H. Critical Comparison Between Gibbs and Duhem

The GPR and the Duhem theorem play complementary roles within thermodynamics. The former establishes the number of independent variables in a system at equilibrium, whereas the latter defines the intrinsic relationships among those variables. Together, they provide a rigorous and comprehensive framework for the analysis of thermodynamic equilibrium.

The GPR and the Duhem theorem are complementary but not interchangeable. The GPR counts independent degrees of freedom at equilibrium, whereas the Duhem theorem constrains the independent variation of intensive variables in a closed system. The Gibbs–Duhem relation then provides a practical differential consistency condition for partial molar properties and activity-coefficient models [12], [13].

This combined perspective improves conceptual clarity and computational traceability: degree-of-freedom counting defines the admissible state description, while consistency relations provide an internal check on constitutive thermodynamic models.

I. Computational Thermodynamics and Model Validation

Modern thermodynamic modeling relies on numerical methods that enforce both GPR and Gibbs–Duhem constraints. These methods include CALPHAD, molecular simulations, and equation-of-state models. Their accuracy depends on both theoretical consistency and high-quality experimental data [10].

Model validation is a critical step in ensuring predictive reliability. Inconsistencies in data or parameter estimation can lead to violations of thermodynamic constraints. Therefore, systematic validation procedures are required [12].

Recent studies demonstrate that enforcing thermodynamic consistency significantly improves model accuracy. This is particularly important in systems with strong non-ideal behavior or multiple interacting phases. As a result, consistency checks are now standard practice in advanced thermodynamic modeling [1].

J. Thermodynamic Simulation Analysis

The calculated T–x–y diagram at 5066.25 kPa shows a composition-dependent equilibrium envelope for the supplied CO_2–methanol working model. Differences between the calculated curves and the reference points reflect the combined influence of the selected correlations, NRTL parameters, and numerical implementation. Because the parameter set was not independently re-estimated in this study, agreement is interpreted as a model-screening result rather than as a validated high-pressure VLE correlation.

The Gibbs–Duhem consistency calculation provides a separate internal check on the NRTL activity coefficients. When the fixed-condition residual remains close to zero, the composition dependence of γ_1 and γ_2 is mutually consistent with (3). This internal test does not, by itself, establish agreement with experimental phase behavior; it only indicates that the activity-coefficient calculation satisfies the selected thermodynamic consistency criterion.

Taken together, the reference-data comparison and the Gibbs–Duhem residual provide complementary information. The first evaluates how the working model reproduces the supplied phase-equilibrium trend, whereas the second evaluates internal consistency of the calculated activity coefficients. Disagreement with reference data can therefore persist even when the consistency residual is small.

The example also illustrates why model selection matters in CO_2 separation calculations. Predictions of phase composition and phase fraction can propagate directly into material balances and process-design calculations. Before quantitative use beyond the conditions shown here, the high-pressure formulation should be independently validated and, where appropriate, compared with a fugacity-based equation-of-state treatment.

IV. FUTURE DIRECTIONS

Future research should focus on extending thermodynamic frameworks to non-equilibrium systems. This includes incorporating kinetic effects, transport phenomena, and time-dependent behavior. Such extensions are essential for accurately describing real-world systems.

Another promising direction is the integration of machine learning with thermodynamic modeling. Thermodynamics-informed and multi-output learning approaches can improve property prediction in high-dimensional systems [22], but

physical constraints such as phase-rule and Gibbs–Duhem consistency must remain explicit validation requirements.

V. CONCLUSION

This study presents an integrated interpretation of the Gibbs Phase Rule, the Duhem theorem, and the Gibbs–Duhem consistency relation. The GPR establishes the structural degrees of freedom of an equilibrium system, while the Duhem theorem limits the independent variation of intensive variables in a closed system. The Gibbs–Duhem relation provides a practical consistency condition for composition-dependent partial molar properties and activity-coefficient models.

The proposed workflow combines degree-of-freedom analysis, equilibrium constraints, and computational consistency checks. Its application to the CO_2–methanol working example demonstrates how an equilibrium envelope, phase-fraction calculation, and Gibbs–Duhem residual can be used together without treating these outputs as equivalent tests.

The simulation also highlights an important modeling limitation: internal thermodynamic consistency does not guarantee quantitative accuracy of a particular high-pressure VLE formulation. Parameter validation, experimental comparison, and an appropriate treatment of phase fugacity remain necessary when predictions are extended beyond the conditions used to construct the model.

The combined framework remains useful for teaching and for screening computational thermodynamic models, particularly because it separates three questions that are often conflated: how many variables may vary independently, how equilibrium constrains those variables, and whether a constitutive model is internally consistent.

Future work should include independent validation of the CO_2–methanol high-pressure model, extension to additional compositions and pressures, and comparison with fugacity/equation-of-state formulations. More broadly, generalized phase-rule treatments, non-equilibrium extensions, and thermodynamics-informed machine-learning models should retain explicit physical consistency checks.

Overall, the study connects classical equilibrium thermodynamics with a reproducible computational example and clarifies the distinct roles of the Gibbs Phase Rule, Duhem theorem, and Gibbs–Duhem relation in modern thermodynamic analysis.

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