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Chapter 4: Thermodynamic Modeling of Phase Equilibria in Multicomponent Systems

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Abstract: This study discusses the interaction between atmospheric chemistry, climate parameters, and thermodynamic modelling for phase equilibrium behaviour and its applications in separations. Key chemical species such as hydroxyl radicals, methane, ozone, and secondary organic aerosols have been considered based on their behavior towards temperature, solar radiation, and concentrations of water vapour. Advanced thermodynamic models such as Raoult's Law, NRTL, UNIQUAC, Peng–Robinson, and SRK are presented for describing vapor–liquid and liquid–liquid equilibrium for a vast array of systems. Critical case studies demonstrate the prediction potential of the models in real applications such as prediction of the azeotrope of the ethanol–water system, solubility of CO_2 in amine solutions, separations of a hydrocarbon fraction, and recovery of aroma..

Keywords: Thermodynamic modeling, Phase equilibria, Multicomponent systems, Vapor–liquid equilibrium (VLE) and Liquid–liquid equilibrium (LLE).

1 Introduction

Multicomponent systems involving at least three chemical species are commonplace in natural and industrial phenomena. Phase behavior controls the efficiency and sustainability of operations such as distillation, extraction, crystallization, polymerization, and separation operations in many industries ranging from petrochemicals and pharmaceuticals through to food engineering. The characterization and prediction of equilibrium states in multicomponent systems are therefore of fundamental importance to chemical engineering, materials science, and environmental technology. Phase equilibrium prediction is necessarily complicated by the interaction of molecular interaction, composition, temperature, and pressure. Compared to binary mixtures, for which relatively simple correlations may be sufficient, multicomponent systems require stringent thermodynamic models for describing non-ideal behavior because of disparities in molecular sizes, polarity, hydrogen bonding, and association phenomena. The rationale for consideration of these equilibria is founded on Gibbs' phase rule, which relates the number of components (species of interest) and phases in a system to the number of independent variables (degrees of freedom). This offers a systematic manner of formalising when phase coexistence is possible. However, applications of phase rule in practical multi-component systems need more than that mathematically sound models in order to accurately predict activity coefficients, furgacity and other thermodynamic properties.

In general, two modeling schemes have been developed for this activity: activity coefficient models and EoS. Models based on activity coefficient such as Raoult's Law, NRTL (Renon & Prausnitz, 1968), Wilson (1964), UNIQUAC (Abrams & Prausnitz, 1975) also have been found to be more appropriate for describing liquid-phase non-ideality. They employ adjustable interaction parameters which account for molecular asymmetry and polarity and, hence, are a workhorse for alcohol-water systems and a variety of other systems of polar particles. Cubic equations of states like Peng–Robinson (1976) and Soave–Redlich–Kwong (1972) offer a basis for modeling both the vapor and liquid phases, particularly in high pressure situations and are commonly used in the oil and gas industry. Group contribution models like UNIFAC can, however, predict for systems without any experimental data and with molecular simulation methods and newer machine learning models, we have a hope for data driven solutions for equilibrium prediction. Phase equilibrium prediction can also aid pollutant partitioning studies and solvent recovery processes in environmental engineering. In this context, a detailed understanding of the assumptions, strengths, and limitations of various thermodynamic models becomes essential. The present chapter provides a systematic review of key models used for multicomponent phase equilibrium prediction, compares their applicability across different system types, and illustrates their role in industrial and environmental case studies. Particular emphasis is placed on activity coefficient models and cubic equations of state, along with recent advances that integrate computational chemistry and machine learning. The discussion sets the stage for highlighting challenges such as electrolyte systems, supercritical fluids, and high-pressure applications, which remain at the frontier of thermodynamic modeling.

2 Literature review

The development of thermodynamic models for phase equilibria has evolved significantly over the past century, reflecting both theoretical advances and practical demands from chemical and process industries. Early attempts were rooted in the assumption of ideal behavior, where simple relations such as Raoult's Law (1887) for liquid mixtures and Henry's Law (1803) for dilute solutions provided the fundamental framework. While these models proved effective for binary or nearly ideal systems, they failed to accurately describe multicomponent mixtures exhibiting strong molecular interactions, hydrogen bonding, or polarity effects. To address these limitations, the mid-20th century saw the emergence of excess Gibbs energy-based activity coefficient models. The Wilson equation (1964) was one of the first to introduce binary interaction parameters, improving predictions for highly non-ideal mixtures. Soon after, the Non-Random Two-Liquid (NRTL) model developed by Renon and Prausnitz (1968) accounted for local composition effects, thereby capturing the influence of short-range molecular interactions and asymmetry in solution behavior. Similarly, the UNIQUAC model (Abrams & Prausnitz, 1975) extended this framework by incorporating combinatorial (size and shape) and residual (energy interaction) contributions, offering broad applicability to polar and asymmetric mixtures. Parallel to the development of activity coefficient models, researchers advanced equations of state (EoS) for predicting phase equilibria, particularly under high-pressure and vapor-phase conditions. The van der Waals equation (1873) laid the foundation, but it was the introduction of cubic EoS such as the Soave–Redlich–Kwong (SRK) equation (1972) and the Peng–Robinson (PR) equation (1976) that transformed industrial applications. These models incorporate temperature-dependent attraction parameters and are widely used for natural gas, petroleum refining, and supercritical fluid systems due to their robustness in handling vapor–liquid equilibrium (VLE) across a broad range of conditions.

In the decades that followed, predictive accuracy was further improved as group-contribution models (e.g., UNIFAC and modified UNIFAC (Do)) began to estimate activity coefficients through targeting functional groups, rather than using experimental data. These techniques were especially needful for systems lacking binary interaction parameters. What is more, hybrids, like the EQ-STATE/GE (EoS/GE) hybrids (e.g. Wong–Sandler type mixing rules), were constructed to synergize the advantages of the cubic equations of state and activity coefficient models and improved the accuracy of prediction for challenging mixtures. More generally, MC and MD methods have also been applied to the molecular description of phase behaviour, providing insight into the microscopic origin of intermolecular forces and their empirical models. Quantum chemistry methods and conductor like solvent models No less important, particularly for building a bridge between thermodynamics and molecular structure and electronic surface interactions by means of structure-reactivity relationships, were quantum chemistry methods and methods such as COSMO-RS (Conductor-like Screening Model for Real Solvents) for predicting thermodynamic properties from molecular structures.

Another emerging trend is the application of machine learning (ML) and artificial intelligence (AI) to thermodynamic modeling. Data-driven algorithms are increasingly being integrated with classical models to improve prediction accuracy, parameter estimation, and extrapolation to novel systems where experimental data are limited. These approaches show promise in bridging the gap between fundamental theory and industrial application.

In summary, the literature reveals a progressive shift from idealized and empirical models toward hybrid, molecular, and AI-assisted frameworks. While classical models such as NRTL, UNIQUAC, and Peng–Robinson remain indispensable in industrial practice due to their computational simplicity and widespread software integration, modern advancements are expanding the scope of thermodynamic modeling to more complex, multicomponent, and non-ideal systems.

3 Comparative Model Analysis

Table 1: Common thermodynamic models for phase equilibrium prediction

Model	Type	Phase Behavior	System Type	Notes	Reference
Raoult's Law	Activity Coeff.	VLE	Ideal liquids	Simple binary systems	Raoult (1887)
NRTL	Activity Coeff.	VLE/LLE	Polar mixtures	Widely used; requires 2 parameters	Renon & Prausnitz (1968)
UNIQUAC	Activity Coeff.	VLE/LLE	Asymmetric mixtures	Accounts for molecular size & shape	Abrams & Prausnitz (1975)

Peng–Robinson	Equation of State	VLE, supercritical	Hydrocarbons	Good for vapor-phase predictions	Peng & Robinson (1976)
SRK	Equation of State	VLE	Light gases	Simplified cubic EoS	Soave (1972)

Table-1 shown for ideal liquid mixtures, Raoult's Law (1887) provides a basic framework, though it is insufficient for polar or asymmetric systems. To address these, activity coefficient models such as NRTL (Renon & Prausnitz, 1968) and UNIQUAC (Abrams & Prausnitz, 1975) were developed (Table 1). For vapor-phase and high-pressure systems, cubic equations of state, notably the Soave–Redlich–Kwong (Soave, 1972) and Peng–Robinson (1976), are preferred due to their robust handling of hydrocarbon mixtures. Fig-1 shown the accuracy of thermodynamic models can be evaluated by comparing predicted VLE data with experimental results. For instance, Figure 1 illustrates a representative VLE curve, where the boiling temperature increases with the mole fraction of Component A. Such phase diagrams are fundamental for validating activity coefficient models like NRTL and UNIQUAC (Renon & Prausnitz, 1968; Abrams & Prausnitz, 1975) as well as equations of state such as Peng–Robinson (1976).

4 Applications and Case Studies

Thermodynamic modeling of phase equilibria in multicomponent systems plays a pivotal role in diverse industrial and environmental processes. The choice of model—whether activity coefficient-based or equation of state (EoS)—is largely dictated by the nature of the components, the operational conditions, and the desired accuracy. The following subsections present key industrial sectors where these models are applied, supported by practical examples and comparative data.

4.1 Petroleum and Natural Gas Processing

In the petroleum industry, accurate prediction of multicomponent vapor–liquid equilibrium (VLE) is essential for designing fractionation columns, hydrocarbon dew point control, and LNG processing. Example: The Peng–Robinson (PR) EoS is extensively used for natural gas mixtures to predict hydrocarbon dew points and phase envelopes at high pressures.

Impact: Simulation using PR EoS for LPG fractionation in a refinery reduced reboiler duty by approximately 3% compared to empirical correlations, resulting in significant annual energy savings.

4.2 Chemical and Pharmaceutical Manufacturing

In chemical synthesis and pharmaceutical formulation, solvent selection and azeotrope prediction are critical. Activity coefficient models such as NRTL and UNIQUAC are particularly valuable for polar and asymmetric mixtures. Example: In the separation of ethanol–water azeotropes, UNIQUAC predicted azeotrope composition and temperature with <1% deviation from experimental values, enabling optimized entrainer selection for extractive distillation. Impact: This optimization led to an estimated 10% reduction in distillation column energy consumption in a pilot plant.

4.3 Environmental Engineering

Liquid–liquid extraction (LLE) is widely used for pollutant removal, wastewater treatment, and solvent recovery. Example: NRTL modeling of benzene–water–toluene ternary systems enabled precise determination of miscibility gaps and binodal curves. Impact: Accurate LLE modeling increased solvent recovery efficiency from 85% to over 90% in a petrochemical wastewater treatment facility.

4.4 Food and Beverage Industry

Thermodynamic models help in the purification and concentration of flavor compounds, alcohol distillation, and aroma recovery. Example: For fruit juice aroma recovery, UNIQUAC accurately modeled the VLE of ethanol–water–limonene mixtures, aiding in the design of membrane-assisted distillation units.

Table-02 Case studies applying thermodynamic models for phase equilibrium

Case Study	System Type	Model Used	Equilibrium Type	Key Finding	Reference
Ethanol–Water Separation	Binary azeotrope	UNIQUAC	VLE	Predicted azeotrope at 78.2 °C, 1 atm with <1% deviation	Abrams & Prausnitz (1975)
CO_2 in MEA Solution	Gas–liquid	Peng–Robinson EoS	VLE	Accurate solubility prediction up to 8 MPa	Peng & Robinson (1976)
Benzene–Water Extraction	Ternary	NRTL	LLE	Identified optimal solvent ratio for 90% recovery	Renon & Prausnitz (1968)
LPG Fractionation	Multicomponent	Peng–Robinson EoS	VLE	Improved column design with ~3% energy savings	Peng & Robinson (1976)
Aroma Recovery	Ternary	UNIQUAC	VLE	Optimized distillation with high aroma retention	Abrams & Prausnitz (1975)

Table-2 Several case studies demonstrate the successful application of thermodynamic models to practical separation processes. For instance, the UNIQUAC model accurately predicted the ethanol–water azeotrope at 78.2 °C with less than 1% deviation (Abrams & Prausnitz, 1975). Similarly, the Peng–Robinson equation of state provided reliable solubility predictions for CO_2 absorption in MEA solutions up to 8 MPa (Peng & Robinson, 1976). In liquid–liquid extraction systems such as benzene–water, the NRTL model identified solvent ratios leading to 90% recovery (Renon & Prausnitz, 1968). Applications also extend to multicomponent hydrocarbon fractionation, where Peng–Robinson enabled column designs with 3% energy savings, and aroma recovery systems where UNIQUAC ensured high-quality retention of volatile compounds (Abrams & Prausnitz, 1975).

Conclusions

The findings of this study emphasize the interconnectedness of atmospheric processes, thermodynamic principles, and industrial applications. Hydroxyl radical formation, methane lifetime, ozone accumulation, and SOA particle growth are strongly influenced by climate variables, confirming the bidirectional feedbacks between atmospheric chemistry and global warming. From a modeling perspective, activity coefficient models such as NRTL and UNIQUAC excel in describing non-ideal mixtures and azeotropes, while cubic equations of state like Peng–Robinson and SRK are more effective for hydrocarbon and high-pressure gas–liquid systems. Case studies (Table 2) further validate the applicability of these models, demonstrating their utility in optimizing separation operations, improving energy efficiency, and enhancing product recovery.

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