

Correlation of Binary VLE by G^E Models: Comparison of Unconstrained Optimization Methods

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Binary VLE data are needed in the design of distillation equipment and for the testing of liquid mixture models. Most of the liquid mixtures encountered in commercial operations are non-ideal. The non-ideality in a liquid mixture can be concisely represented by the Excess Gibbs Energy ($G^E/RT = g^E$). There are several empirical and semi-theoretical models proposed in the literature. Correlation of P–T–x–y data consists of determining the constants in the G^E models by minimizing the objective function $\sum (g_{\text{exp}}^E - g_{\text{cal}}^E)^2$. The constants can be obtained by several methods, which may be classified as (a) methods based on solution of sets of non – linear equations; and (b) methods based on optimization techniques.

The g^E models proposed in literature can be classified as (a) single parameter; (b) two parameter; and (c) multi-parameter models. The g^E models can be broadly classified as classical models and models based on the local composition concept. Often they are classified as enthalpic models, entropic models, and complete g^E models ($g^E = h^E - TS^E$).

In this paper, four methods of unconstrained optimization namely Nelder–Mead, Steepest Descent and Genetic Algorithm are selected for estimation of parameters in the isothermal binary VLE data of the system hexafluorobenzene (1) / benzene (2) at 333.15 K using several g^E models (about 40), and the results of processing the data are presented.