Thermodynamic Consistency Testing of VLE Data via the Gibbs-Helmholtz Equation

James Olson [C, S]
MATRIC (Mid-Atlantic Technology, Research & Innovation Center), Charleston, WV, U.S.A.
olson.wv@suddenlink.net

The objective of thermodynamic consistency tests is to show the likely absence of systematic errors. The practical uses are (i) to referee between different data sets on the same system, (ii) to justify confidence in the chemical process equipment designed from the data, and (iii) to ensure data of the highest quality for experimental standards and for testing and extension of theory. Binary PTxy (pressure-temperature-liquid mole fraction-vapor mole fraction) vapor-liquid equilibrium (VLE) data are redundant according to the phase rule. Hence, differential and integral thermodynamic consistency tests can be constructed from the Gibbs-Duhem equation. In contrast, Px or Tx (PTx) data are the minimum necessary to specify VLE so that the Gibbs-Duhem tests are not possible. However, G^E data derived from PTx data measured at several temperatures can be compared to calorimetric H^E data with the Gibbs-Helmholtz equation,

$$-RT^2[\partial(G^E/RT)/\partial T]_{P,\{x\}} = H^E$$

This comparison can be used as a thermodynamic consistency test for PTx data.

Results are presented for Gibbs-Helmholtz analysis of ebulliometrically-determined PTx data for the systems water + acrylic acid, 1, 2-propylene glycol + ethylene glycol, 1, 3-propylene glycol + ethylene glycol, and water + N-methylethylenediamine. The system ethanol + water is revisited to demonstrate the effects on Gibbs-Helmholtz analysis from using a local-composition model with fixed temperature dependence instead of using a Redlich-Kister expansion at each temperature. In addition, the special Gibbs-Helmholtz problems presented by nearly-ideal systems are analyzed.