

A Generalized Form of the Redlich-Kister Equation

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A 1948 paper by Redlich and Kister was a landmark exposition that set the stage for the “algebraic representation of the thermodynamic properties and classification of non-electrolyte solutions”. The primary aim of the paper was “efficient utilization of laboratory data for the design of distillation columns” and was, consequently focused on the development of power series expansions for excess free energy and activity coefficients. The Redlich-Kister (RK) equation derives its strength from the fact that higher-order terms are corrections to lower-order terms, which works out like a convergent series with a finite number of terms. The RK equation is, thus, a powerful mixing rule form which can take on higher-order terms (allowing the incorporation of additional interaction parameters) necessary for correlation of the composition-dependence of non-ideal liquid mixtures, e.g., density, enthalpy, and viscosity. Furthermore, the advent of modern-day densitometers and similar instrumentation, has added a large body of high-precision liquid mixture thermophysical property data, also requiring multiple interaction parameters to correlate within measurement uncertainty, which can similarly be furnished by the RK equation. Consequently, over time, the RK equation has become the correlation of preference for the applied thermodynamics research community. Recently, Sen and co-workers have demonstrated a technique employing virial-based mixing rules to describe the composition dependence of liquid phase thermophysical properties. This investigation illustrates the basic strategy embodied in these mixing rules, as well as a slightly modified version which is shown to be a generalized form of the RK. Results for the RK equation and the virial-based mixing rules are compared. The easy extension of the virial-based mixing rules to multi-component mixtures (alleviating a key weakness of the RK equation) is also demonstrated.