

# Thermodynamic Consistency and McMillan-Mayer Scale Conversion in Multisolvent Electrolyte Solutions

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The conversion of activity coefficients and osmotic coefficients between the McMillan-Mayer (MM) framework (comprising most electrolyte theories) and the Lewis-Randall (LR) framework (including most experimental data) is carefully investigated. Two methodologies are presented: (1) the conversion based on the Kirkwood-Buff solution theory, and (2) thermodynamic principles (e.g., the Poynting correction).

We pay special attention to conversion in multisolvent electrolyte solutions, since its theoretical status is not clearly known, and the industrial importance is great. We clarify the relation between the single-solvent case and the multisolvent case. Formulas valid in the former may not be valid in the latter.

We develop molecular interpretations whenever possible. The Gibbs-Duhem relation, basis of thermodynamic consistency, is analyzed in both the Lewis-Randall and the McMillan-Mayer frameworks. A new hybrid formula is derived that allows the proper inclusion of MM quantities into the LR picture. Furthermore, we propose the use of the affinity principle “halophilia” and “halophobia” regarding the solvents to construct useful equations for solvent activity calculations.