

A Thermodynamically Sound and Numerically Robust Modelling Framework for Mixed Aqueous Electrolyte Solutions and for Redefining pH

Eric May^{1, S, C} and Peter May²

¹*Engineering, The University of Western Australia, Crawley, Western Australia, Australia*

²*Chemistry, Murdoch University, Murdoch, Western Australia, Australia*
eric.may@uwa.edu.au

At present the Pitzer equations are the only credible theoretical framework for modelling the thermodynamics of multicomponent chemically reactive aqueous electrolyte solutions over a range of concentrations. For this reason, they are currently being used in a major international research project to describe the predominant chemical equilibria in seawater and to improve the quantification of pH changes, important for understanding uptake of atmospheric CO₂ and ocean acidification. Unfortunately, the Pitzer framework suffers from appreciable theoretical and numerical limitations, which undermine such modelling efforts. Among other issues, obtaining reliable values for the necessary Pitzer equation parameters is a large, and largely thankless, task.

An alternative aqueous thermodynamic modelling paradigm has now been developed and will be described. It is simpler than the Pitzer framework, conforms fully with the constraints of thermodynamics, is easier to parameterise, is more numerically robust, and follows satisfactorily the empirical mixing rules of Harned and of Young. It also avoids certain theoretical inconsistencies which appear in the Pitzer equations for asymmetric electrolytes.

The new framework has been used to describe within reasonable uncertainty the data of many strong electrolyte systems at 1 bar / 25 °C, where the literature values have been taken from our JESS databases, including:

- (i) over 20,000 individual mean ionic activity coefficients, osmotic coefficients, apparent molar volumes and apparent molar heat capacities for more than 200 single strong electrolyte solutions;
- (ii) over 10,000 individual mean ionic activity coefficients, osmotic coefficients, apparent molar volumes and apparent molar heat capacities for about 100 common-ion mixtures; and,
- (iii) over 10,000 conditional equilibrium constants, measured for reactions in an aqueous medium as a function of background salt concentration.

Importantly, through a rigorous description of single ion activity coefficients, the new framework provides a better basis than the Pitzer equations or SIT for quantifying chemical reaction equilibria in aqueous solutions and for defining pH. How the latter may be achieved in practice is outlined in an associated presentation.