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to measure the free energy of a solution of sodium ions. However, single-ion thermodynamics becomes accessible when nonclassical techniques such as atomic and molecular spectroscopy are combined with statistical mechanics. In modern practice, quantum mechanical theory is often able to replace spectroscopic observations, and that also broadens the range of species that can be characterized thermodynamically.

Even though most scientists intuitively understand the breakdown of classical prohibitions, the technical issues surrounding the broadening of classical thermodynamics still engender controversy. For single-ion solvation, an ideal theoretical interpretation would include a free energy that reflects the interaction of a solute with an infinite solvent that has no boundary. But experimentalists inevitably measure a contribution associated with the electrical work of an ion crossing the dipolar vapor–liquid interface. Extrathermodynamic considerations, which may be either experimental or theoretical, are therefore required to estimate the surface term, and the estimates vary widely, by as much as 1 eV/ion (roughly 100 kJ/mol), with even the sign sometimes uncertain. Discussions of that surface effect can be confusing even to experts and can become heated (even though the effect itself is isothermal).

Single-Ion Solvation: Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities by Philippe Hünenberger and Maria Reif offers the best discussion I've seen of the subject's complexities and subtleties. The book's careful explanations should make its readers much more comfortable in tackling the thorny issues; it can even make a previously confused person like me confident enough to write a book review. It is hard to overemphasize the high quality of the writing. Often, after making a statement, the authors anticipate myriad possible misinterpretations or overgeneralizations and clear them up one by one. I was also favorably impressed by the 2406 references listed in the book.

The authors conclude, perhaps controversially, that even though the surface term can be estimated from experiments, such estimates are uncertain, mainly because “*bulk and surface effects are simply not unambiguously partitionable.*” They further conclude that the ambiguous partitioning affects all single-ion thermodynamic properties,

though that's not surprising since all thermodynamic properties can be written as functions of the free energy and its derivatives.

Single-Ion Solvation is clear and lighthearted. The book is illustrated with clever cartoons. I enjoyed the authors' wry comment about the large number of extrathermodynamic assumptions that have been advocated: “They always sound intuitively reasonable, at least to their author.” But they do not lose sight of the serious implications of single-ion solvation, and they conclude that the numerous approaches and their associated conventions and often ambiguous specifications are “a constant source of mistakes in the field.” A clear understanding of the material in this book would minimize those mistakes.

The authors make a number of recommendations, such as the use of “real” and “intrinsic” to distinguish free energies that respectively do and do not include the surface term. I prefer that approach to avoiding mention of the issue or using the ambiguous term “absolute” or the jargon term “galvanic.” I also heartily agree with their observation that physical interpretation is more straightforward for what they call semi-standard point-to-point solvation parameters (as opposed to standard-state ones): They distinguish those quantities by a large and a small circle, respectively, in the state symbol, whereas in my own papers I employ the notations ΔG_s^* and ΔG_s^0 . That might be the only place in the book where I think the pedagogy can be improved: The authors never point out that ΔG_s^* corresponds to solvation in a surface-free fluid at a fixed concentration (the same number of moles per liter in the vapor and in solution). Among other benefits, fixed-concentration solvation has a clearer physical interpretation than standard-state solvation because, as emphasized by physical chemist Arieh Ben-Naim, under such conditions the entropy of translation in the vapor equals the entropy of liberation from a fixed point in solution. Therefore, the free-energy change can be directly related to the work of coupling the solute to the solvent.

One thing I did not like about the book is that many tables are printed in a small font and therefore hard to read. Also, the text font itself is small and light, at least in my copy. The publisher should do a better job.

For aficionados, *Single-Ion Solvation* is a little bit like a mystery book; it

leaves readers anticipating what values the authors will ultimately recommend for key quantities. Spoiler alert! For an aqueous solution, they recommend a surface potential of +0.13 V, and for a proton in water, an intrinsic semi-standard point-to-point solvation free energy of –265 kcal/mol.

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Single-Ion Solvation

Experimental and Theoretical Approaches to Elusive Thermodynamic Quantities

Philippe Hünenberger
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Classical thermodynamics is a beautiful subject. Albert Einstein famously said that it “is the only physical theory of universal content which I am convinced will never be overthrown.” Indeed, scientists are confident that we will not observe any violation of the first and second laws of Rudolf Clausius's thermodynamics, even after we admit the post-Clausius realities of relativity, atomic structure, and quantum mechanics.

But other firm prescriptions of classical thermodynamics are not on such solid ground. For example, it is possible in the context of classical thermodynamics to measure the free energy of a solution containing sodium chloride, but because electroneutrality must be attained in bulk matter, it is impossible

