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Abstract

The current status of thermodynamic modelling in aqueous chemistry is reviewed. A number of recent developments hold considerable promise but these need to be weighed against ongoing difficulties with existing theoretical modelling frameworks. The current modelling paradigm evidently has to be re-assessed, hopefully to find better ways forward, including new protocols which command sufficient support to warrant IUPAC endorsement. Some key issues are identified and discussed.

INTRODUCTION

Thermodynamic modelling is required routinely to understand the relevant solution chemistry in numerous and wide-ranging applications of environmental, industrial and biomedical importance. Such investigations encompass carbon uptake by the oceans,¹⁻³ ocean acidification and its effects,^{1,4-7} storage repositories for CO₂(g)⁸ and radionuclides,⁹⁻¹² heavy metal pollution,¹³⁻²¹ wastewater treatment,^{20,22} desalination,²³⁻²⁵ scale formation,²⁶⁻²⁹ gas scrubbing,^{30,31} minimising corrosion,^{21,32,33} hydrometallurgical and other industrial process optimisation,³⁴⁻⁴⁰ urinary kidney-stone drug design,^{41,42} chelation therapy⁴³ and general bioinorganic understanding.^{44,45}

This paper reviews the current status of aqueous chemistry thermodynamic modelling for such applications. Our aim is to identify and discuss crucial current aspects of the subject, rather than attempting to be comprehensive. Many of these issues are most evident when modelling simple synthetic solutions but, unsurprisingly, they apply also to more complicated mixtures like seawater, urine and blood plasma even though they may then be more surreptitiously hidden. To summarise the topic succinctly but, at the same time, provide non-specialists with sufficient supporting information from the chemical literature, we give some details separately at the end of the paper in the Appendix.

PROMISING RECENT DEVELOPMENTS

It can hardly be questioned that computerisation has provided the greatest technical impetus to science in general since World War II. It is commonplace to recognise that computers are now deeply embedded in instrumentation as well as providing extremely powerful tools in their own right. In ways that would previously have been unimaginable, they have enabled the powerful and pervasive application of mathematics to science; they have led to the development of large-scale molecular simulation capabilities of various kinds; and, they have revolutionised the collection, storage and processing of experimental data and associated modelling parameters. All these accomplishments bear heavily on the present subject. In aqueous chemistry, as in thermodynamics generally, major recent advances unrelated to some form of computing have on the contrary been relatively scarce.

The physical chemistry of aqueous solutions, which before World War II had engaged many of the finest contemporary scientific minds, established an enormous base of knowledge and data (see the texts of Lewis and Randall,⁴⁶ of Harned and Owen,⁴⁷ and of Robinson and Stokes,⁴⁸ in particular). Adding to this effort was the burgeoning research that, through the genius of L.G. Sillén, commenced in the 1950s at KTH in Stockholm (Sweden). Unsurpassed in coverage, coherence, and experimental rigour, almost all the major pillars of modern solution chemistry were brought to a fine art and, from there, disseminated around the world. Computers provided an obvious means to cope with all this new scientific information: the stability constant compilations of Sillén and Martell,^{49,50} for instance, provide a cornerstone for many subsequent thermodynamic databases in solution chemistry (*e.g.* refs 51-54). Although Sillén and co-workers were not the first to apply computers to multicomponent thermodynamic calculations (that involved the determination of

gaseous products at equilibrium formed during rocket fuel combustion⁵⁵⁻⁵⁸), they were pioneers in both thermodynamic modelling⁵⁹ and experimental data analysis;⁶⁰ they were indeed the earliest researchers working in any branch of science to refine the parameters of their mathematical models by least-⁶⁰ and they warned, even then, against the risks of over-estimating the significance of the answers obtained!

It was against this formative background as a student of Robin Stokes at the University of New England, Armidale, NSW, Australia that Ken Marsh built his initial interests in thermodynamics, data accumulation and computing. This led in due course to his appointment as Director of the TRC (Thermodynamics Research Center) at Texas A&M and his support for their first electronic database.⁶¹ insistence on high quality in experimentation, evaluation, publication and data assessment will be a significant part of his enduring legacy.

Effective application of such information technology remains the best hope for future thermodynamic calculations in aquatic chemistry. Nowadays, S⁶²⁻⁶⁴ and⁶⁵ are well-proven tools. Making the most from information processing includes taking greatest advantage from modern experimental techniques and addressing the modelling difficulties that still confront us. Exploiting the great potential of dielectric relaxation spectroscopy (DRS) as a probe for niggling weak ion pairing interactions in aqueous solution (see Appendix), is a good example (especially now that the significance of the Debye-Falkenhagen effect^{66,67} has been recognised⁶⁸). DRS has a unique ability to address some of the most intractable aspects of the modelling difficulties outlined below and dealt with in ref 69. A second important example would be the recently improved focus on errors where they arise, how they are transmitted and what impact they have. to speed calculations.⁷⁰ Error propagation issues plague thermodynamic modelling in part because they have previously been so neglected; they are now at least becoming better recognised, although a lot still remains to be done.^{71,72}

automatically evaluate all data supplied, automatically remove or correct errors, and automatically return the best set of fitted parameters for the chemical species in a given system. Evaluation of experimental data must, by its very nature, be an interactive process between the compiler and the

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Advances in computer technology are undoubtedly leading to large-scale thermodynamic databases of ever-improving quality. The pioneering efforts by the U.S. National Bureau of Standards (NBS) and its successor the National Institute of Science and Technology (NIST) and by CODATA⁷³ to assemble critically-assessed thermodynamic data are being continued through both the OECD Nuclear Energy Agency (NEA)⁷⁴⁻⁸¹ and through the International Union of Pure and Applied Chemistry (IUPAC),⁸²⁻⁸⁴ involving vital international collaboration, expert assessments and peer review. However, it is only through the use of computers that there can be progress in assembling the vast numbers of necessary data, systematising and preserving it such that, through methodical detection and correction of errors, overall quality improves faster than human fallibility can reduce it.⁸⁵⁻⁸⁷ To think this observation is trite is probably to be unaware of early history with thermodynamic databases (see ref 88 and references therein). Maintaining internal consistency in large thermodynamic datasets is a formidable undertaking in which automation is the only realistic

possibility, particularly given the limited resources of personnel . Various computational approaches to achieve and sustain thermodynamic consistency have at last begun to mature (refs 12, 87, 89 95 and 81, p 35)¹⁵ and^{3,96} are expected to be given more attention. On the other hand, this proliferation of disparate thermodynamic databases itself already needs some sort of (unifying?) plan for the future.

The improved quality of readily-available physicochemical data has been remarkable given the poor contributions from some major compilers prior to the year 2000 (Figure 1). Tomes such as those by Aseyev and Zaytsev^{97 99} are rife with inconsistencies. Even the widely-used reference work for aqueous solution densities by Söhnel and Novotný¹⁰⁰ has significant discontinuities between adjacent pages in the original publication for the same substance, *e.g.* H₂SO₄(aq)!

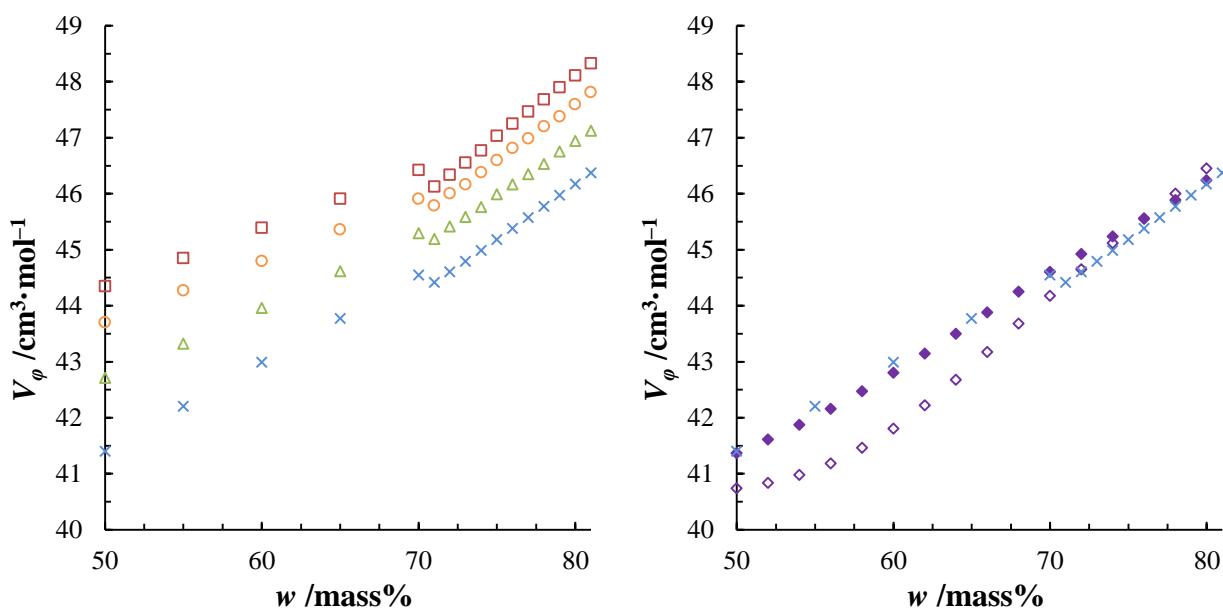


Figure 1. Left: Reference data from Söhnel and Novotný¹⁰⁰ for H₂SO₄(aq) showing an artefactual discontinuity when plotted as the apparent molar volume, V_ϕ , versus concentration in weight percent, w (g solute / 100 g solution), at 10 °C (blue crosses, bottom), 30 °C (green triangles), 50 °C (orange circles) and 70 °C (red squares, top). Right: Comparison of reference data plotted as apparent molar volume, V_ϕ , versus concentration in weight percent, w , at 10 °C; from Söhnel and Novotný (blue crosses) and from Aseyev and Zaytsev⁹⁹ set 1 (filled diamonds) and set 2 (open diamonds).

There are many reasons for the improvements to databases that are increasingly manifest. Computers have greatly reduced the burden of unit conversion *etc.*, they can be used to check for careless mistakes, they can impose thermodynamic conformance, they can take advantage of thermodynamic redundancy to improve reliability, and they can be easily applied to smooth and unify experimental data, by averaging and other numerical methods. The limitations of data derived

from a single laboratory, no matter how reputable, are increasingly being appreciated and their implications better understood.^{101,102} We have noted a particularly valuable feature of precise empirical equations like those of Pitzer and Hückel (which often give closely similar results for various thermodynamic functions) for unifying data from multiple sources (Figure 2) and identifying systematic errors. Elimination of experimental outliers in mixed solutions of strong electrolytes has also been made much easier by the systematic corroboration and subsequent application of so-

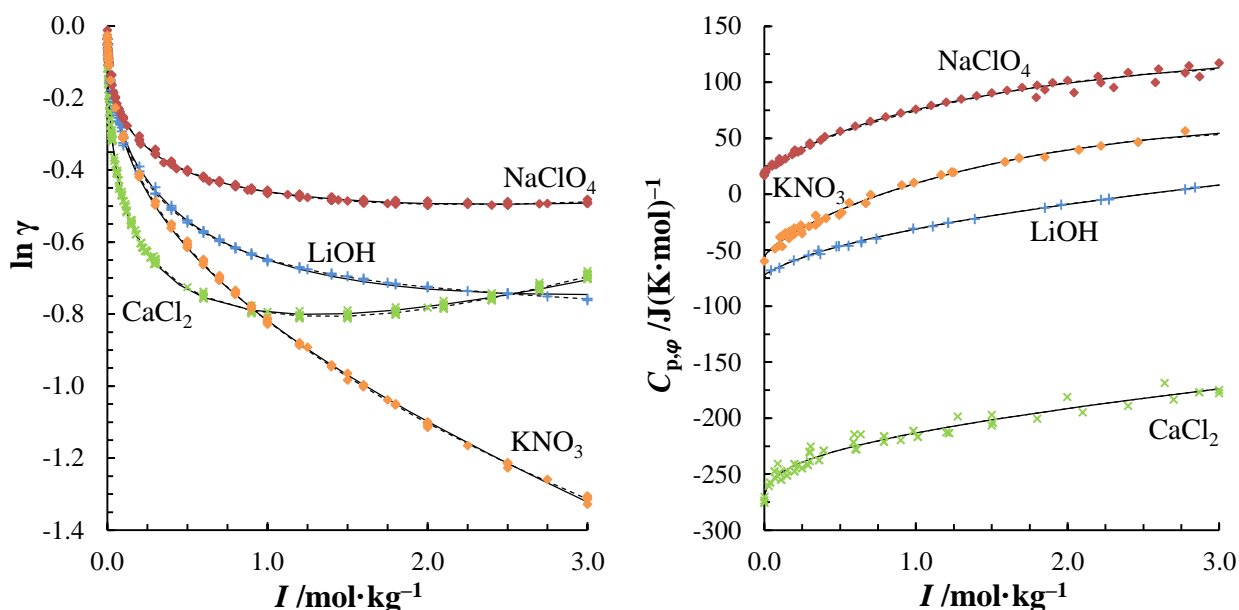


Figure 2. Physicochemical property data for $\text{NaClO}_4(\text{aq})$, $\text{LiOH}(\text{aq})$, $\text{CaCl}_2(\text{aq})$ and $\text{KNO}_3(\text{aq})$ fitted almost identically by both the Pitzer (solid lines) and the Hückel (dashed lines) equations. Left: Activity coefficients plotted as natural logarithms, $\ln \gamma$, versus ionic strength, I , in $\text{mol}\cdot\text{kg}^{-1}$. Right: Apparent molar heat capacities, $C_{p,\phi}$, in $\text{J}\cdot(\text{K}\cdot\text{mol})^{-1}$ versus ionic strength, I , in $\text{mol}\cdot\text{kg}^{-1}$. Data and fitting facilities are from the JESS software package.^{92,104}

Phase diagrams for innumerable multi-component systems are now appearing in the literature (see refs 105–108 for recent examples). While the reliability of the thermodynamic models used to describe these systems is, for the purposes of prediction, often questionable (as described in the next Section) the rejection of bad data is greatly facilitated by the regression analyses performed in such studies. In other words, it is easier to identify inconsistent results based on thermodynamic modelling than it is to make true predictions (*i.e.* without relying on tailor-made fits). Eliminating

paves the way to finding better theoretical explanations, which might otherwise be obscured by undetected systematic errors.

Topical issues associated with $\text{CO}_2(\text{g})$ dissolved in aqueous solutions have also attracted considerable attention, especially regarding solubility.^{72,109–112} There has been special interest in the

general importance of electrolyte interactions,¹¹³ scrubbing technologies,^{114,115} potential scale-formation,^{110,116,117} modelling chemical processes in rock pore waters,^{118,119} the exploitation of saline aquifers for carbon capture and storage^{120 127} and ocean acidification.^{1,7,128} Such investigations typify the need for generalised thermodynamic modelling capabilities in aqueous chemistry for simulating the variety and complexity of the many prospective practical applications.

THERMODYNAMIC MODELLING FRAMEWORKS - UNRESOLVED DIFFICULTIES

Two decades ago, Loehe and Donohue¹²⁹ summarised the then current status of thermodynamic property modelling of aqueous electrolyte systems in these words:

successful approach to strong electrolyte thermodynamics, it is not easy for the nonspecialist to choose among them for estimating given properties. In addition, the equations often are complex, and using them correctly often requires the expert advice and assistance of their formulators. Thus, there is a need for a critical comparison of the performance of published equations for electrolyte thermodynamic properties with each other and with available experimental data. While there is a large selection of equations for mean ionic-activity coefficients, there are fewer choices for accurate

Unfortunately, many of these issues persist,¹³⁰ hindering the task of thermodynamic modelling in aqueous reactive systems. The vast majority of well-characterised reactions in aqueous solution have had their thermodynamics quantified by the methods pioneered at KTH, namely, in the

using such background electrolytes (typically $\text{NaClO}_4(\text{aq.}, 3 \text{ mol.dm}^{-3})$) was to study chemical equilibria including metal-ligand complexing reactions under conditions that ensured the constancy of the activity coefficients for the interacting species. In other words, the reactions could then be characterised in terms of so-called activity quotients of species concentrations rather than of activities. This obviated the need for a good activity coefficient model (which was not available at the time). Unfortunately, these conditional constants are strictly inapplicable to other electrolyte compositions, a mis-match that becomes acute with weak chemical equilibria (see Appendix) and which frames the backdrop to many unresolved issues in solution chemistry.

The modern authoritative doctrine on modelling in aquatic chemistry was laid out under the auspices of the OECD Nuclear Energy Agency (NEA) in the book edited by Grenthe and Puigdomenech,¹³¹ which stands in conjunction with a series of NEA recommendations and critical literature reviews including most recently a volume on the solution thermodynamics of iron.⁸¹ This colossal project, driven by the needs of nuclear waste management, has assembled dozens of specialists from all over the world to provide definitive statements on the state of the art and current best practice. It is firmly rooted in the solution chemistry tradition developed at KTH and strongly emphasises scientific objectivity, quality and reliability. The conclusion of the NEA team, in a nutshell, is that the only pragmatic way to model most systems of interest depends on the SIT (Specific Ion Interaction

Theory) Equation (1). IUPAC also endorses the SIT approach in its ¹³² and a number of critical reviews of stability constants.⁸²⁻⁸⁴ Complementing the pedigree of SIT even further is the Bates-Guggenheim convention, a Debye-Hückel equation that takes the form of Equation (1) (with $\varepsilon(i, k) = 0$ for all electrolytes in dilute solutions^{133,134}) and which is currently employed in the definition of pH.

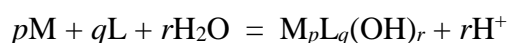
Specific Ion Interaction Theory

SIT offers a simple equation for the calculation of activity coefficients (ref 135, p 332):

$$\ln \gamma_i = -\frac{z_i^2 A \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + \sum_k \varepsilon(i, k) m_k \quad (1)$$

Equation (1) yields a notional single-ion activity coefficient, γ_i , for a target ion i in the presence of another ion, k . The first term describes the contribution from a Debye-Hückel theory extension and the second term gives the specific effect between ion i and ion k at molal concentration m_k based on a short-range interaction coefficient, $\varepsilon(i, k)$. A is the constant for activity coefficients in the Debye-Hückel limiting law with a value 1.1743 (= 0.5100 × ln 10) mol^{1/2}·kg^{1/2} at 25 °C and 1 atm, lower-case z is the charge on the ion, and I_m represents the ionic strength in mol·kg⁻¹.

As stated verbatim in the latest IUPAC Technical Report,⁸⁶ when Equation (1) is applied to the general reaction (omitting charges except for H⁺)



p, q, r , and that determined in an ionic medium of ionic strength I_m , p, q, r , is

$$z^2 D \log_{10} a(H_2O) = \sum_k \varepsilon(i, k) m_k$$

The value of D is defined by the activity coefficient relationship on the molality scale for a single ion i by

$$m(i) = \frac{z_i^2 A \sqrt{I_m}}{1 + a_i B \sqrt{I_m}} + \sum_k \varepsilon(i, k) m_k = z_i^2 D + \sum_k \varepsilon(i, k) m_k$$

in which k is M or X or L or N , i, k corresponding to that in Equation (1) above is given by

$$\varepsilon(i, k) = \begin{cases} + & \text{or } X \\ +, X & \\ n+, X & \\ m, N+ & \end{cases}$$

The activity of water expressed in the term $\log_{10} a(H_2O)$ can be calculated from the solution osmotic coefficient.

Although they recommend the SIT approach, Grenthe *et al.*¹³⁵ also place numerous strictures on the use of Equation (1). These include doubts from assuming $\varepsilon(i, k)$ is independent of concentration (p 332); an artificial requirement that $\ln \gamma_+ \equiv \ln \gamma_-$ in all pure strong n:n electrolytes arising from the symmetry in defining $\varepsilon(i, k) \equiv \varepsilon(k, i)$ (p 333); other issues associated with single-ion activity coefficient expressions tied to electroneutral combinations of ions (p 331); and, the implicit adoption of the Brønsted principle of specific ion interaction^{136,137} asserting that $\varepsilon(i, k) = 0$ between two cations or two anions (p 333). This concept may be satisfactory in dilute solutions as Brønsted intended it; however, the principle implies that the interaction occurs *via* a change in the (single ion) activity coefficient of the counter-ion and this presumes implicitly that the interaction comes about from an ionic *attraction*. Representing two like-charged ions as repelling one another directly is an alternative at higher concentrations which seems much more obvious when $\ln \gamma_{\pm}$ is increasing.

Far from establishing a reliable and universal protocol for general purpose thermodynamic modelling of aqueous solutions, deficiencies in current capability are thus merely underscored by the NEA recommendations. Worst of all for general modelling purposes are the serious inaccuracies of the SIT equation in predicting the properties of *pure* strong electrolyte solutions (*i.e.* the binary systems with just one salt and water). The equation fails in many cases due to the fixed value of 1.5 in the denominator of the Debye-Hückel term (see Figure 1 of ref 138). In essence, this means that SIT can only be applied sensibly to chemical systems with reactions taking place at low concentrations¹³⁹ and/or in a swamping concentration of a so- (see above). Unfortunately, since systems with many ingredients such as seawater, hydrometallurgical liquors and biofluids typically exhibit an awkward spread of component concentrations, this restriction compromises the generality and accuracy of SIT models in many practical applications. Also, determining the chemical speciation in pure solutions, *i.e.* difficult and hence mostly remains beyond current capability.

Pitzer's equations

The only widely-used alternative to SIT at present is the Pitzer framework. This offers unparalleled precision in correlating the thermodynamics of strong electrolyte solutions over a broad set of concentrations and conditions. Proven by common experience, the Pitzer equations^{140,141} work well for numerous binary (one salt plus water) systems (refs 142, p 39 and 143), and also for mixtures, as long as there are sufficient experimental data of high quality available for parameterisation. They have accordingly been adopted for the full characterisation of NaCl(aq) and KCl(aq) thermodynamic properties by the U.S. National Institute of Standards and Technology^{144,145} and for the best thermodynamic description of various other aqueous strong electrolyte systems by a host of independent investigators.

On the other hand, there are serious difficulties with the Pitzer equations that are inherent in the virial expansion on which the equations are based and from which stem their empirical (refs 104

and 142, p 61) accuracy. In particular, the Pitzer framework lacks reliability and is prone to fail badly when there are gaps or other deficiencies in the fitted experimental data. It is well known, for example, that the Pitzer equations are much less robust than SIT (ref 135, p 365). Pitzer parameters determined in sets are prone to subsequent inconsistencies and ongoing revision – see ref 146 for instance. Fortunately, these and other limitations are now becoming better understood.¹⁴⁷ A key point to remember is that gaps are the rule, not the exception, when optimising parameters for multicomponent systems. Therefore, the greater the number of empirical adjustments, the less robust the solution will be. Adjusting dozens of variables to describe systems with only a few species^{148,149} or *five or more* variables for a single, pure aqueous electrolyte under isothermal conditions^{150,151}

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Although conceived originally for just strong electrolyte systems, the Pitzer equations can in principle be applied to any chemically-reactive multicomponent solution. Unfortunately, notwithstanding some particular monumental efforts,^{153 156} it is currently prohibitive to couple Pitzer-like frameworks with large-scale chemical speciation calculations. This is because the numerous parameters it requires cannot feasibly be determined experimentally.¹⁵⁷ Attempts to solve the problem by various methods of parameter estimation have been described^{158 161} but such initiatives generally consider only the simple reactant species (*e.g.* metal and ligand ions) and they fail to address the product species (*e.g.* complexes), which actually represent the main challenge.

Predicting the properties of multicomponent mixtures without sound methods for parameter estimation is fraught with risk. Grenthe *et al.*¹³⁵ conclude that when Pitzer parameter values are unknown, the quality of data reproduction and predictions deteriorates, with the loss of any advantage over the SIT approach (p 365). They emphasise the dangers of using extensively-parameterised Pitzer models,¹³⁵ regardless of the good fits to selected experimental data that such models can display (p 366). The unavoidable bottom line is that, like SIT, the use of Pitzer equations *for general purpose modelling of aquatic systems* is flawed and impractical.

Many of these incurable difficulties are associated with the traditional notional representation of single ion activity coefficients (SIACs), which in operation characterises neutral electrolytes, not ions, and is consequently unworkable and unrealistic. Then again, SIACs are a tricky matter which, promoted by much misunderstanding and a surprising number of admitted mistakes, has morphed over the last decade into an ordeal for the solution chemistry community.¹⁶² Nevertheless, an effective SIAC function is needed to deal with the large number of electrolyte permutations that arise in multicomponent reactive mixtures. It must be realistic not only to accord with modern precepts in solution chemistry but also to assist with parameter estimation. And, as Bates¹⁶³ recognised while developing SIT, *only through universal adoption can arbitrary procedures be truly effective.*

Commercial Frameworks

The other theoretical frameworks for modelling aqueous thermodynamics worth mentioning are HKF (named for its originators Helgeson, Kirkham and Flowers),^{164 166} MSE (for Mixed-Solvent Electrolyte)^{167 171} and eNRTL (for Electrolyte Non-Random Two Liquids).^{172 175} These frameworks are employed commercially (HKF/MSE in the OLI Systems package, eNRTL in the Aspen® process simulator) but, relative to the conventional Pitzer equations, have otherwise received little independent corroboration. HKF was embraced enthusiastically early on but this has been followed by disillusionment and declining popularity despite its commercial implementation. Neither HKF as originally formulated nor eNRTL are a match for the Pitzer equations in terms of accuracy, or regarding diversity of the electrolyte systems covered, or of proven track record. Moreover, they are subject to various criticisms concerning their theoretical coherence, as follows.

Studied systematically by Harned and co-workers but amply confirmed by independent investigators it is now beyond doubt that trace activity coefficients are a key property in solution

electrolyte solution mixing has just been confirmed by a comprehensive and up-to-date analysis.¹⁰² While trace activity coefficients are evidenced mainly in mixtures, where they can be derived by extrapolation based on the general pattern of linear behaviour, they also apply to activity quotients of reactions at equilibrium in the presence of a constant electrolyte medium (ref 135, p 326 7]. **Models incapable of explicit trace activity coefficient prediction should therefore no longer be regarded as credible.** Until now, to our knowledge, only the Pitzer equations^{143,176} and the Scatchard model^{177 179} plausibly calculate activity coefficients at trace concentrations distinct from those in the bulk. (The SIT equation can do so too in principle (ref 135, p 360) but it is not recommended for systems requiring more than one adjustable parameter (ref 135, p 333), which precludes its use with most binary electrolytes!¹³⁸ The HKF approach can do no better than attribute

on¹⁶⁷ may help. With eNRTL, a claim regarding trace activity coefficients was made in the original paper¹⁸⁰ but this was unsubstantiated experimentally and it appears subsequently to have been forgotten.^{181 183})

Overarching all these individual imperfections of existing frameworks is another pervasive issue: general purpose thermodynamic modelling of aquatic systems needs to utilise a vast base of knowledge about chemical reactions. An enormous number of interactions occur in almost any chemically-reactive multicomponent assembly. Only chemical speciation frameworks can even aspire to accommodate all of them. To our knowledge, the only substantial chemical property databases integrated into full-scale thermodynamic modelling packages are the commercial offerings from OLI Systems and Aspen®, the IUPAC facility WinSGW linked to SIT¹³² and our own Joint Expert Speciation System (JESS),^{63,88,92} all of which are based on the chemical speciation

by the spurious chemical species (mostly very weak ion pairs)⁹² that have, regrettably, so often been reported in the literature and which are so difficult to resolve experimentally (see Appendix). In generalised thermodynamic modelling, this often proves ruinous because inconsistencies creep into sets of parameters that have been determined simultaneously but are not strictly maintained when they are kept in large databases and later applied to other chemical contexts. It is important to appreciate that just getting rid of these minor species is not the answer either: they represent real

effects (albeit artefactually) which can be important under certain conditions.⁹² Poor handling of changes in electrolyte medium as described above is a related but parallel, and equally serious, complication. Consequently, values predicted for the physicochemical properties of multicomponent systems like seawater (see Appendix) tend often to be grossly inaccurate unless they are fitted to match the answer.

Model fitting

¹⁸⁴ (a euphemism for expedient, one-off, application-specific parameterisation) has become standard practice. It is empirical, usually subjective and sometimes downright implausible. It is the antithesis of what thermodynamics ought to be about. The problem of tailoring answers to suit particular systems is exacerbated by the unfettered possibility of having additional chemical species, like weak ion pairs, omitted to grossly tamper with the answer.

Quantitatively-accurate empirical modelling equations for activity coefficients are, for various reasons, confined to prohibitively narrow contexts: *e.g.* the equations of Hückel,¹³⁸ Pitzer and inherently unsuited to modelling the chemical speciation of multicomponent systems. The Scatchard equations are even less convenient than those of Pitzer.¹⁹³ As a result, thorough integration of either the Pitzer or the Scatchard equations with the vast body of thermodynamic data available for chemical reactions in aqueous solution^{52,194} seems forever beyond reach.

Thermodynamic modelling of aqueous solutions for general purposes therefore remains profoundly difficult and in sharp contrast to internally-consistent calculations for equilibrium systems characterised experimentally at constant ionic strength in a background electrolyte medium. De Visscher and Vanderdeelen¹⁹⁵ carefully document a specific but illuminating instance. However, nothing unveils the predicament more than the large number of different theoretical approaches that have been, and continue to be, described in the literature along with the frequent need for many of them subsequently to be extended or modified (for example, refs 196–204). There is general confusion implicit in having a multitude of ostensibly different, competing theoretical frameworks, some associated with major computer simulation packages but many just popping up in the literature as transient distractions. Few of these –

– *numerical verification* that the composition of phases and their proportions estimated by any thermodynamic solver are calculated in accord
³⁷ Even worse, perhaps, the practice of

contrary to the hope that Loehe and Donohue expressed almost 20 years ago.¹²⁹ Such one-sided advocacy of hypothetical proposals contravenes scientific desiderata.²⁰⁵ The inherent pitfalls of

described at length by Nordstrom.²⁰⁶ The common notion that a newly-proposed model only has to fit the data with a minimum number of adjustable parameters is at best naïve: regression analyses can be used to reject hypotheses but not to substantiate them – a truism that deserves much wider appreciation, especially from journal referees.

It is important finally to note that in modelling aqueous systems, usefulness is certainly not precluded by these various theoretical difficulties. The main purpose of modelling should always

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does require maturity to realize that models are to be used, ²⁰⁷ It is often possible to elucidate the main factors of what goes on in complicated systems from simple models,

a good simplification is a big advantage – as a matter of fact it is a pre- (ref 208, p 15). The only questions are whether the model represents the key elements of the system or not and, then, how accurately does it do so *for the required purpose*. There is an abundance of freely-available speciation modelling software using different databases and different activity coefficient expressions which can be used to examine the sensitivity of calculations to these variables. The essence of good modelling practice is to test the assumptions involved and their relevance to the questions being asked. This is all the more necessary since certain phenomena can cancel, or balance each other out, as is evident from

recurrent numerical correlations. (Indeed, it seems that overlapping fundamental effects in solution chemistry are especially prone to such effects.). Good activity coefficient values are therefore not always critical. At the same time, however, a significant overlooked, particularly when analytical quantifications, accurate property predictions or any significant extrapolations are involved.

CONCLUSION

The abundance in solution of all species must be known to calculate quantities determined by, or thermodynamically related to, γ_{\pm} . However, this chemical speciation cannot be unequivocally determined without a good model for activity coefficients. It has proved impossible to escape this vicious circle without a sound *fundamental understanding* of specific ion interactions.^{209 211} The inadequacies of modelling frameworks described above have not been fixed for this reason.

Even cursory inspection of patterns in activity and osmotic coefficient data shows they are resplendent with anomalies. Kunz and Neuder²¹² describe at length the complicated maze of property relationships, and absence of universal correlations, that arise more generally from specific ion interactions. It appears that every ion finds at least one counter ion that causes a distinct increase in $\ln \gamma_{\pm}$ and at least one other that causes a distinct decrease! While chemical trends within certain series, such as the alkali metal ions, are obvious, finding any explanation, or even pattern, that applies to *all* strong electrolytes has so far proved impossible. While this suggests that there may be more than just one important underlying cause of specific ion interactions, the fact that almost every electrolyte system behaves so straightforwardly, especially when being mixed with others, stands as a striking paradox. Until this paradox can be resolved, efforts can only be directed towards improving our current empirical thermodynamic modelling practices.

Our existing modelling paradigm needs to be re-assessed, hopefully to find better ways forward, including protocols that command sufficient support to warrant IUPAC endorsement. Expertise that is international, authoritative, and disinterested must be held paramount.

should always be acknowledged and minimised. Recognition of the uncertainties in data that have not been confirmed by independent measurement needs to be redoubled. Even the treatment of pH demands repair – as important as it is, pH remains analytically untraceable (see refs 3, 96, 132, 134, 213 215) on account of an ambiguous and controversial definition. Nothing epitomises the prevailing difficulties with SIACs more than this imbroglio. An authoritative recommendation by the International Union of Pure and Applied Chemistry (IUPAC)²¹⁶ pH is unique amongst physicochemical quantities ... in that, in terms of its (notional) definition ... involving as it does a single-

be used which are inappropriate at higher electrolyte concentrations ($>0.1 \text{ mol}\cdot\text{kg}^{-1}$). These problems with pH interpretation are closely associated with limitations in the treatment of liquid junction potential corrections, both experimentally and theoretically. Even recently there has been an emphatic declaration that pH as a measure of the single ion activity of H^+ is undefinable and of no practical benefit²¹⁷ but others^{96,218 220} do not share this opinion.

On the contrary, we consider that the present impasse can be resolved by a fundamentally-sound single-ion activity coefficient function that couples strong electrolyte thermodynamics with weak electrolyte equilibria, allowing multicomponent systems to be modelled with confidence on the basis of reliable mixing rules and better methods of parameter estimation. We believe that the recent work of the Vera group,²²⁰ now coming to grips with SIACs through potentiometric measurements using cells with liquid junction, points the way forward.

models started to appear. The evidence that strong electrolytes are fully dissociated at infinite dilution is overwhelming and includes of independent ion migration, other physicochemical measurements, and even the success of the Debye-Hückel limiting law. At higher concentrations, the implication of the outstanding conductivity work by Palmer, Ho and colleagues^{228 236} at super-ambient temperatures is compelling: all trace of ion pairing in NaCl(aq) and KCl(aq) vanishes when their distinctly-observed effects of ion pairing are extrapolated back to 25 °C.

There is thus a growing body of evidence that in *strong electrolyte solutions* very little association between cation and anion occurs under ambient conditions, even when the metal ion has a strong tendency to form complexes. NiCl₂(aq) and MgCl₂(aq) are good examples where a new X-ray absorption study corroborates long-established knowledge from UV-Vis spectrometry regarding the prevalence of the aquo-ion and the difficulty of forming chloro-complexes.²³⁷ The results to date from dielectric relaxation spectroscopy (DRS) lead us (but not everyone) to a similar conclusion, mainly by way of their generally unsupportive inference.^{68,238} Eiberweiser *et al.*⁶⁹ provide an exemplary case study of just how challenging weak ion associations can still be, prudently reporting their (very small) K^0 estimates as upper limits. Note the contrast when association is found entirely as expected⁶⁹ compared to other systems.^{239,240} However, regarding almost all traditional investigations of weak interactions in aqueous solution, there is a diabolical paucity of good methods.

Direct experimental measurements of chemical speciation are thwarted by practical problems. Specific ion interactions and ion pairing equilibria are indistinguishable when the effects are weak and most techniques yield frustratingly ambiguous results.²⁰⁹ Historically, UV-Vis spectrometry has been one of the most dependable techniques for detecting speciation in aqueous solutions. Unfortunately, the systems of greatest interest are rarely suited to UV-Vis, which mostly only detects species with chromophores forming contact ion pairs.^{68,241,242} Speciation results inferred from fits to experimentally-determined activity and osmotic coefficients (*e.g.* refs 243 249) are often muddled, tend to be self-referencing, prone to major revision and are questionable in principle because good fits are a necessary but insufficient condition for determining chemical speciation. Unfruitful too have been molecular dynamics and quantum simulations (*e.g.* ref 250), often because of inadequacies in representing the complexities of the solution phase at ambient temperatures and intermediate concentrations. So, when an association interaction between ions has an equilibrium constant, K_A^0 , less than about 50, little can yet be said with confidence about the identity or abundance of the individual chemical entities in solution. To make matters worse, how the conditional equilibrium constants, K_A' , vary with increasing concentration has been widely neglected (Smithson and Williams²⁵¹ and De Visscher and Vanderdeelen¹⁹⁵ being exceptional). Unless there is solid, multi-faceted evidence for the existence of a chemical species, in contrast to predictions of it for different contexts and conditions, such species ought to be questioned and, to explain observed deviations against experimental data, other plausible alternatives carefully considered.

ACKNOWLEDGEMENT

Our thanks are due to Glenn Hefter (the Chemistry Department, Murdoch University) and Kirk Nordstrom (U.S. Geological Survey, Boulder) for their constructive comments which helped to improve this manuscript. Most notably, we have included additional coverage on the SIT Equation for chemical reactions (GH) and on the usefulness of some freely-available modelling software despite the current difficulties with theory (DKN), additions which are (of course) our full responsibility.

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