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JESS, a Joint Expert Speciation System – IV: A large database of aqueous solution physicochemical properties with an automatic means of achieving thermodynamic consistency[☆]

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ABSTRACT

The JESS software package, which is a widely-used tool for modelling chemical speciation in complex aqueous environments, has been extended to allow comprehensive predictions of physicochemical properties for strong electrolytes in aqueous solution. Another large database, this time of physicochemical property data, has been added to the JESS suite, along with the computational methods which automatically turn these diverse literature data into a thermodynamically-consistent calculation for water activities, densities, heat capacities, etc. Given the recent emphasis on the role of water activity in predicting electrolyte mixing behaviour, we expect that this capability will lead to major changes in the way aquatic chemistry is modelled in future.

1. Introduction

In the context of aqueous solutions, the term 'chemical speciation' means characterisation of the identity and abundance of every physicochemically-distinct entity present at the molecular level. Calculations of chemical speciation are therefore important both to validate analytical probes and to represent the results of analytical measurements.

It has recently become clear to us that such chemical speciation calculations, especially those dealing with concentrated electrolyte solutions, must utilise the thermodynamic water activities of the solutions more than has been the case hitherto [2]. This and the following paper [3] describe two developments which now permit the water activities, and other thermodynamic properties, to be calculated for a wide array of electrolytes and their mixtures over broad ranges of concentration, temperature and pressure.

In the final stage of characterising thermodynamic systems, great effort must always be put into a coherent representation which describes and predicts the physical and chemical properties of interest. Ideally, a single algebraic summary (i.e. a mathematical model) is needed to embody all the relevant experimental information and any necessary selections and critical assessments of the data. Mathematically speaking, this means carefully weighting the reported experimental results, establishing a particular basis set, elaborating the corresponding functions and properly determining the numerical values of every associated parameter.

However, production of a large-scale, thermodynamically-consistent framework of property parameters requires substantial resources. Thus, this work is traditionally undertaken by dedicated experts, often collaborating in teams, to produce comprehensive and authoritative tabulations. In this way, reliable reference data are published by organisations such as the U.S. National Bureau of Standards/National Institute of Standards and Technology [http://srdata.nist.gov/solubility/], the OECD Nuclear Energy Agency [4–6] and IUPAC (through some of its major collective projects [7–10]). The results of such labour-intensive reviews often underpin impressive secondary sources [11].

Unsurprisingly, such major thermodynamic projects are seriously limited by the resources they require. This problem is exacerbated because the outcome tends to build up progressively from a foundation which fixes the results of each successive layer of work and which, once in place, cannot usually be adjusted without starting again. The enormity of the general challenge is well illustrated by the prodigious efforts of Krumgalz et al. just to characterise the volumetric behaviour of single-solute aqueous electrolyte solutions [12,13]. As a further specific example, consider what happens to published thermodynamic datasets with

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[☆] Part III is Ref. [1].

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constants for aqueous solutions having a standard state based on infinite dilution when, say, the properties of water are re-evaluated, changing the Debye–Hückel constant as a function of temperature. In other words, in developing thermodynamically-consistent descriptions of chemical systems, good additional experimental measurements arriving after the event cannot easily be incorporated. This can even render the entire preceding effort obsolete if the experimental ranges of conditions are significantly extended or if the measurement differences are sufficiently large. Other issues are that it is difficult to correct any errors made early on in the evaluation process and that with increasing complexity, all these problems escalate, making characterisation of multicomponent systems especially troublesome.

For these reasons, achieving thermodynamic consistency by automatic means is a growing imperative. However, this is much easier said than done – the task requires a myriad of decisions, judgements, and comparisons as well as numerical finessing, scientific knowledge, chemical insight and technical skill [14]. Thus, for the foreseeable future, it seems likely that considerable human expertise will still be needed (see 'Section 8').

Grappling with this challenge, nevertheless, has driven the development of our JESS (for Joint Expert Speciation System) software package [15]. JESS is a widely-used tool for modelling chemical speciation in complex aqueous environments [http://jess.murdoch.edu.au], with the largest integrated database of thermodynamic parameters for chemical reactions [16] and an expert system capability for automatically achieving thermodynamic consistency [14]. A philosophy has been evolved and implemented based on the desire to model chemical speciation in aqueous solutions generally and comprehensively. This is necessary to deal with large multicomponent systems such as blood plasma [17], seawater [18] and hydrometallurgical liquors [19,20]. A key principle is to assemble as much of the relevant information as possible into substantial databases, including expertly-assessed scores and other criteria for decision making, and thereafter to perform automatically all the operations leading to a thermodynamically-consistent model. This allows new data to be added, errors to be corrected and judgements to be changed without much ado.

The developments described in this paper concern the comprehensive prediction of physicochemical properties for strong electrolytes in aqueous solution. Measured data, as much and as varied as possible, together with the harmonising power of thermodynamics, are used to achieve the objective. Our approach is again founded on a large and growing database – this time of physicochemical property data – along with the computational methods that automatically turn diverse literature sources into a thermodynamically-consistent calculation for water activities, densities, heat capacities, etc. Given recent emphasis on the role of water activity in predicting electrolyte mixing behaviour [2], we expect that having water activities available for as many electrolyte solutions over as wide a range of conditions as possible, will lead to major improvements in the way aquatic chemistry is modelled in future.

2. The physicochemical property database

The JESS physicochemical property database (FIZ) stores quantities for measured thermodynamic properties of bulk aqueous solutions under well-defined conditions of composition, temperature and pressure. Most of the data concern simple electrolytes, but non-electrolyte solutes such as dissolved gases and other neutral molecules are also accepted. All recorded values are associated with so-called 'merit weights' between 0 and 9 to reflect their assessed reliability.

At present, the database contains values for over two dozen physicochemical properties (Table 1).

The current symbols for electrolytes are given in Table 2.

Activity coefficients, osmotic coefficients, densities/molar volumes, apparent molar relative enthalpies and solubilities are the most common of these properties. Although there is a long way still to go, currently more than 175,000 property values have been recorded, with the data spanning about 120 electrolytes. In line with the JESS approach developed for reaction data [14,16], values from both primary and secondary sources are included. (This strategy aims to make JESS models robust and relatively more stable in response to adjustments of the data; all data are treated simply as 'information content' of assessable worth, thus being capable of contributing to knowledge of how each system behaves but allowing evolutionary change to occur when necessary.) Rejected data are likewise also included in the FIZ database but are assigned zero weight so that they have no effect on any subsequent processing. (This minimises the waste of effort associated with bad data which, when not recorded in databases of this kind, are prone to be repeatedly re-discovered, re-assessed and re-rejected.)

The system design allows for many more physicochemical properties than that are currently recognised, each having up to 1 million values for any given solute and property (with NaCl expected to comprise the largest data sets). There can be up to 45 recognisable cations, 45 recognisable anions and 35 recognisable non-electrolyte substances. There is a current design upper limit of 10,000,000 values per physicochemical property.

The FIZ database is constructed in two phases: (a) the assembly and input of critically-assessed literature data for the various properties into computer sequential files formatted for readability and (b) the conversion of these data into computer direct access files for rapid retrieval, display and processing. A systematic layout for the data in sequential files has been designed to deal with binary (one solute in water) and ternary (two solutes in water) solutions. Much routine analytical expertise has also had to be encoded, particularly regarding the interconversion of measurement units and thermodynamic quantities. This is critical to process data which are deliberately stored (and displayed) in a way that matches the literature source as closely as possible rather than in the converted, unified form ultimately needed for mathematical regression.

Various subtle problems must be overcome at this early FIZ stage. For example, there is a need for recursion when, say, a function for solution density is in the process of being determined but the data have been measured in concentration units which must be converted using the solution density itself. Similarly, the water activities of certain electrolytes used for reference purposes in isopiestic studies, need to be available to process many isopiestic data. It suffices to say that with the power of computers now available, almost all such issues have been, or can progressively be, resolved.

3. The specific interaction parameter database

The JESS specific interaction parameter database (SIP) is a generalised facility for storing the coefficients of, and evaluating, specific-interaction functions such as are used in the Bronsted–Scatchard–Guggenheim specific interaction theory (SIT) [22,23] and Pitzer [23,24] models for electrolyte solution thermodynamics. These coefficients can be taken directly from the literature with few limitations or they can be evaluated from the FIZ data as described below.

The significance of the SIP database is that it provides a convenient mechanism for managing the large number of Pitzer and SIT parameters necessary to describe the many electrolyte solution properties that have been experimentally characterised. It is

Table 1
FIZ-recognised physicochemical properties[a].

Property name	Default unit	Other units
Mean activity coefficient	Unitless	
Trace activity coefficient	Unitless	
Single ion activity coefficient	Unitless	
Mean activity coefficient ratio[b]	Unitless	
Water activity	Unitless	
Boiling point elevation[c]	°C	K
Boiling point	°C	K
Apparent molar compressibility	/GPa	
Apparent molar heat capacity, *Cp*	J/(K mol)	cal/(K mol)
Volumetric heat capacity quotient[d]	J/(K cm^3)[e]	
Specific heat capacity	J/(K g)	J/(K kg); cal equivs.
Specific heat	J/g	
Apparent molar heat capacity, C_v	J/(K mol)	cal/(K mol)
Compressibility	/GPa	/Mbar
Absolute density	kg/m^3	g/cm^3
Relative density difference	kg/m^3	g/cm^3
Relative density quotient	Unitless	
Specific gravity	Unitless	
Apparent molar expansivity	/kK	
Expansivity	/kK	
Freezing point depression[c]	°C	K
Freezing point	°C	K
Molar excess Gibbs energy	kJ/mol	kcal/mol; J/mol; cal/mol
Apparent molar relative enthalpy[f]	kJ/mol	kcal/mol; J/mol; cal/mol
Apparent molar enthalpy of dilution[g]	kJ/mol	kcal/mol; J/mol; cal/mol
Integral molar enthalpy of dilution[h]	kJ/mol	kcal/mol; J/mol; cal/mol
Apparent molar enthalpy of mixing	kJ/mol	kcal/mol; J/mol; cal/mol
Apparent molar enthalpy of solution[g]	kJ/mol	kcal/mol; J/mol; cal/mol
Molar excess enthalpy	kJ/mol	kcal/mol; J/mol; cal/mol
Isopiestic H_2SO_4 concentration	mol/kg	
Isopiestic $CaCl_2$ concentration	mol/kg	
Isopiestic KCl concentration	mol/kg	
Isopiestic NaCl concentration	mol/kg	
Osmotic coefficient	Unitless	
Osmotic pressure	Pa	MPa; KPa; Torr; atm; bar
Partial molar solvent heat capacity	J/(K mol)	cal/(K mol)
Partial molar solute heat capacity	J/(K mol)	cal/(K mol)
Harned cell potential difference[i]	V	mV
Concentration cell potential difference[j]	V	mV
pe	Unitless	
pH	Unitless	
Partial molar solute enthalpy	kJ/mol	kcal/mol; J/mol; cal/mol
Partial molar solvent enthalpy	kJ/mol	kcal/mol; J/mol; cal/mol
Partial molar solute entropy	J/(K mol)	cal/(K mol)
Partial molar solvent entropy	J/(K mol)	cal/(K mol)
Partial molar solute volume	cm^3/mol	m^3/mol
Partial molar solvent volume	cm^3/mol	m^3/mol
Solubility/saturation limit[k]	mol/kg	M; g/L; %w/w; %w/v
Molar excess entropy	J/(K mol)	cal/(K mol)
Specific volume	cm^3/g	m^3/kg
Apparent molar volume	cm^3/mol	m^3/mol
Vapour pressure	Pa	MPa; kPa; Torr; atm; bar
Molar excess volume	cm^3/mol	m^3/mol

[a] The FIZ interface distinguishes between three different kinds of physicochemical property. There are (a) properties of the bulk solution such as the absolute density and the heat capacity, (b) properties defined in terms of the solvent as the implicit component in question such as the water activity and the osmotic coefficient and (c) properties defined in terms of a solute in solution such as activity coefficients and solubilities.

[b] $\gamma\pm(P,T,c)/\gamma\pm(1\text{ atm.}, 25\,^\circ\text{C}, c)$.

[c] As a difference w.r.t. to H_2O.

[d] As measured, for example, by flow calorimeters.

[e] Quotient is, of course, unitless but this gives the scale.

[f] Apparent molar relative enthalpy at given P, T(HA) $= L_\phi = H_{P,T} - H^0_{P,T}$ is the preferred property (rather than the molar enthalpy of the solution, H, and the molar enthalpy of the solution at infinite dilution, H^0, themselves); L_ϕ should only be computed using H and H^0 values from the same source to maintain internal consistency and limit error propagation associated with the taking of differences between two similar values. $L_\phi = 0$ at infinite dilution for all temperatures, by definition.

[g] Initial and final solution concentrations given for single electrolyte solutions diluted with water.

[h] $\Delta H_{ID} = H_\phi(m_{final}) - H_\phi(m_{initial})$ [21].

[i] For the cell without LJP: Pt, H_2(g, P bar) | HX(m_1), MY(m_2) | AgCl, Ag.

[j] For the conc. gradient cell with transference: ref. electr. | MX(m_1) | MX(m_2) | ref. electr.

[k] Refers to saturated solutions of the subject component or of a recognised solid phase.

Table 2
FIZ-recognised ionic components.

Cation	Anion
Aluminium(III), Al^{3+}	Acetate
Ammonium, NH_4^+	Aluminate, $Al(OH)_4^-$
Barium(II), Ba^{2+}	Arsenate, AsO_4^{3-}
Beryllium(II), Be^{2+}	Arsenite, AsO_3^{3-}
Cadmium(II), Cd^{2+}	Borate, $B(OH)_4^-$
Calcium(II), Ca^{2+}	Bromate, BrO_3^-
Cerium(III), Ce^{3+}	Bromide, Br^-
Cesium, Cs^+	Butyrate, butanoate
Chromium(II), Cr^{2+}	Carbonate, CO_3^{2-}
Chromium(III), Cr^{3+}	Chlorate, ClO_3^-
Cobalt(II), Co^{2+}	Chloride, Cl^-
Cobalt(III), Co^{3+}	Chromate, CrO_4^{2-}
Copper(II), Cu^{2+}	Cyanide, CN^-
Europium, Eu^{3+}	Dichromate, $Cr_2O_7^{2-}$
Gadolinium, Gd^{3+}	Dihydrogenphosphate, $H_2PO_4^-$
Hydrogen ion, H^+	Ferricyanide, $Fe(III)(CN)_6^{3-}$
Iron(II), Fe^{2+}	Ferrocyanide, $Fe(II)(CN)_6^{4-}$
Iron(III), Fe^{3+}	Fluoride, F^-
Lanthanum(III), La^{3+}	Formate
Lead(II), Pb^{2+}	Hydrogencarbonate, HCO_3^-
Lithium, Li^+	Hydrogenmalonate
Magnesium(II), Mg^{2+}	Hydrogensuccinate
Manganese(II), Mn^{2+}	Hydrogensulfate, HSO_4^-
Mercury(II), Hg^{2+}	Hydroxide, OH^-
Neodymium, Nd^{3+}	8-Hydroxyquinolate, oxinate
Nickel(II), Ni^{2+}	Iodate, IO_3^-
Potassium, K^+	Iodide, I^-
Praseodymium(III), Pr^{3+}	Malonate
Rubidium, Rb^+	Molybdate, MoO_4^{2-}
Samarium, Sm^{3+}	Monohydrogenphosphate, HPO_4^{2-}
Scandium(III), Sc^{3+}	Nitrate, NO_3^-
Silver(I), Ag^+	Nitrite, NO_2^-
Sodium, Na^+	Oxalate
Strontium(II), Sr^{2+}	Perchlorate, ClO_4^-
Tetra-n-butylammonium, Bu_4N^+	Permanganate, MnO_4^-
Tetraethylammonium, Et_4N^+	Phosphate, PO_4^{3-}
Tetramethylammonium, Me_4N^+	Phthalate
Tetra-n-propylammonium, Pr_4N^+	Propionate, propanoate
Thallium(I), Tl^+	Pyrophosphate, $P_2O_7^{4-}$
Uranyl, UO_2^{2+}	Silicate, $SiH_2O_4^{2-}$
Yttrium(III), Y^+	Succinate
Zinc(II), Zn^{2+}	Sulfate, SO_4^{2-}
	Thiocyanate, SCN^-
	Thiosulfate, $S_2O_3^{2-}$
	Triflate, $CF_3SO_3^-$

critical to keep track of the parameter sets determined by optimisation and to be able to locate and apply them efficiently when needed for property calculations.

To this end, the SIP database associates each set of parameters with a label for the so-called 'equation variant', i.e. a name given to indicate the source of the parameter set.

4. Development of the JESS optimiser for physicochemical data

JESS optimisation of the physicochemical data for *binary* electrolyte solutions characterises physicochemical properties using the Pitzer formalism. The Pitzer equations are general, effective and widely used for describing thermodynamic data, especially in highly concentrated solutions [23]. A particular advantage of the Pitzer equations, over the Hückel equations [25–27] for example, is that the former are parametrically linear, and hence are suited to standard numerical procedures for solving linear least-squares problems.

Every optimisation begins with the extraction from the FIZ database of a data set that matches specified property and condition limits. To find the Pitzer parameter values, the equations are then cast in a form suitable for singular value decomposition (SVD) [28]. SVD allows best-fitting parameters to be found even when the fitting matrix is ill-conditioned, which can be a significant issue with Pitzer equations [29]. Particular care must be taken not to overfit any data set since this leads to a decrease in predictive power.

The selection of functions allowed by the optimiser has been limited as a guide to achieving general, reproducible and consistent results. The following set of functions has been chosen as adequately representative of models in the literature [30,31] which have analytic derivatives. The form of the general expansion for the excess Gibbs energy, activity coefficient or osmotic coefficient is given by

$$X = \sum_{i=1}^{3}\sum_{j=1}^{7} x_{ij} f_i(P) g_j(T)$$

$$f_1 = 1, \quad f_2 = P - P_r, \quad f_3 = P^2 - P_r^2$$

$$g_1 = 1, \quad g_2 = \frac{T_r}{T}, \quad g_3 = \ln\left(\frac{T_r}{T}\right), \quad g_4 = T - T_r, \quad g_5 = T^2 - T_r^2$$

$$g_6 = \frac{1}{T_U - T} - \frac{1}{T_U - T_r}, \quad g_7 = \frac{1}{T - T_L} - \frac{1}{T_r - T_L}$$

where X is one of the Pitzer parameters β^0, β^1, β^2, or C^{φ}, and x_{ij} are the optimised coefficients, with each parameter then expanded as a function of temperature and pressure. P_r and T_r are the reference pressure and temperature respectively. T_U and T_L are temperatures close to the upper and lower critical values for water. From this form, the parameter expansions are readily manipulated to obtain equations for volumetric and thermometric properties. Up to 95 fitting parameters are thus available for SVD optimisation. Recommended selections of parameter sets, which depend on the range of conditions spanned by the data, are generated automatically but can be overridden by user-specified parameter sets if so desired.

The properties that have so far been included in the optimisation process are activity and osmotic coefficients, relative apparent molar enthalpy, apparent molar heat capacity and apparent molar volume. As discussed in Ref. [24], these properties are the most directly applicable for identifying the Pitzer parameters and their derivatives. When the heat capacity or molar volume is included in the optimisation the standard state (infinite dilution) value of the respective property is also needed. These standard state quantities must in turn be parameterised to determine their variation with pressure and temperature. For example, the standard state heat capacity used in this work takes the following form.

$$C_P^0 = c_0 + c_1(T - T_r) + c_2(T^2 - T_r^2) + c_3\left(\frac{1}{T_U - T} - \frac{1}{T_U - T_r}\right) + c_4(P - P_r) + c_5(P^2 - P_r^2)$$

where the c_i are fitted coefficients. (Various other approaches are possible here and these remain under ongoing investigation.)

Direct comparison between multiple optimisations for the same electrolyte with different data sets is made using a normalised chi-square statistic. By reporting just the worst-fitting data points, significant outliers can be identified and then flagged as rejected in the database. This contributes to a progressive refinement of critical assessments recorded in the FIZ database. A noteworthy example occurred with the activity coefficient data of LiCl reported in Ref. [32]. When these data were entered into the FIZ database and optimised, several values at 75 °C and one value at 50 °C could be seen as seriously anomalous so their weights could be set to zero. Another example is the data from Ref. [33] for the osmotic coefficient of NaCl between 20 and 90 °C, which generally appear inconsistent with other data (such as those from Refs. [30,34–37]). The least-squares optimisation procedure is particularly sensitive to the presence of outlying data. It follows that predictions for

Table 3
Example of the JESS analysis[a] for a single physicochemical value.

γ	FIZ file location	Merit weight[b]	Reference
0.675	AC22A/479	7s	Partanen and Covington [27]
0.670	AC22A/62	3s	Harned and Owen [34]
0.66818	AC22A/379	5s	Zemaitis et al. [37]
0.668	AC22A/137	3s	Robinson and Stokes [35]
0.669	AC22B/17	6s	Pitzer et al. [30]
0.67079	AC22C/94	7s	Archer [38]
0.668	AC22A/207	5s	Hamer and Wu [39]

[a] FIZ data shown are for NaCl(aq) solution (2,000 m, 25 °C, 1 bar). For optimisation, a total of 480 activity and osmotic coefficients were obtained from the FIZ database (0.001–6.144 m, 25 °C, 1 bar). The Pitzer equation coefficients determined with the Bradley–Pitzer formula for the Debye–Hückel parameter [40] were $\beta^0 = 0.07833$, $\beta^1 = 0.2683$ and $C^\phi = 0.0008629$, yielding an activity coefficient $\gamma = 0.6713$. The worst-fitting point in the optimisation occurred at 1.4 m with $\gamma = 0.662$ from the extended Hückel equation of [27] compared to the value calculated from the JESS-fitted Pitzer equation, this being $\gamma = 0.6576$.

[b] Merit weights indicate both a score between 0 and 9 for assessed reliability (see text) and either ‘p’ or ‘s’ for primary or secondary data respectively.

the NaCl system (in this case) progressively improve as aberrant data are assigned low or no weight during subsequent optimisation cycles.

5. Case study 1

Partanen and Covington [27] have very recently reported an authoritative re-evaluation of the thermodynamic activity quantities in aqueous sodium chloride solutions, NaCl(aq), at 25 °C. Their results were entered into the FIZ database and the relevant data re-processed. This immediate incorporation of newly-available data provides a good example of the JESS facilities described here and an interesting illustration of the issues arising for aquatic chemistry modellers keen to use the best, most up-to-date values. Table 3 summarises the process as it pertains to a single data point for this given electrolyte solution at fixed concentration, temperature and pressure.

Given that NaCl(aq) under ambient conditions is surely characterised thermodynamically best of all electrolyte solutions, the differences evident in the third significant figure, whilst small, cannot be regarded as negligible. However, it seems to us that the precise value which might be critically selected out of this range of results, all from highly reputable sources, would be a matter of opinion more than of good judgement. This opinion depends in part on the view one takes about the respective advantages of the Hückel and the Pitzer equations. Whichever of these equations is preferred, however, we are comfortable with today’s JESS-determined outcome of $\gamma = 0.6713$. Should future measurements support the higher value just proposed by Partanen and Covington, the merit weights of the earlier data sets will be progressively reduced and hence the JESS-determined value will gradually increase; alternatively, if not, the JESS process will have avoided an excursion over time, away from and then back towards the cluster of the older values.

Similar issues arise when the electrolyte data sets are not as well characterised as NaCl(aq) so that the consequences of changes over time become harder to understand. For instance, some significant differences occur even with the activity coefficients of KCl(aq) at 25 °C and 1 bar for which there are excellent primary data. The discrepancy is most notable at 1.8 m where Partanen and Covington [27] recommend $\gamma = 0.584$ compared with Hamer and Wu [39] who give $\gamma = 0.576$.

The magnitude of such problems is typically greater still with electrolytes other than NaCl(aq) and KCl(aq). This is important since there is then the potential to alter thermodynamic modelling outcomes, often substantially.

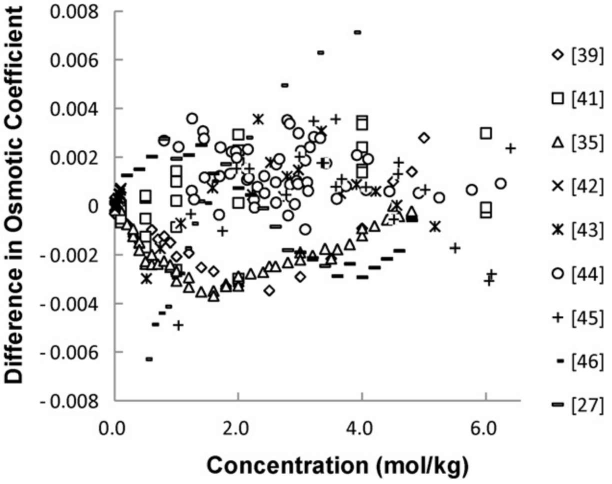

Fig. 1. KCl(aq) deviations of osmotic coefficient data from the Pitzer model.

6. Case study 2

The JESS optimiser for physicochemical data was used to generate a model from 702 thermodynamic data points for aqueous solutions of potassium chloride, KCl(aq), in the range 0–100 °C, 0–6.56 m and 1 bar. The optimised data included activity and osmotic coefficients [27,35,39,41–46], apparent relative molar enthalpies and apparent molar heat capacities [21,41,47–50]. Fig. 1 shows the deviations of osmotic coefficients obtained from the automatically produced model. The available data and the fit achieved by the Pitzer functions are very satisfactory in this case. Most of the osmotic coefficient data are reproduced to within ±0.002, with only a few outliers outside ±0.004. Fig. 2 shows the deviations achieved for the heat capacity data. As would be expected from the experimental uncertainty, the largest deviations occur with data approaching infinite dilution but the remainder are mostly within ±7 J/(K mol).

The noticeable disagreement between measured values at low concentration and the Pitzer model in this case study is symptomatic of the difficulty in representing the extreme temperature dependence of the infinite dilution standard state. Accurately modelling the apparent molar heat capacity at infinite dilution, in particular, has been discussed by Archer [38,41] who has used a finite reference molality, a sensible feature which we have yet to implement.

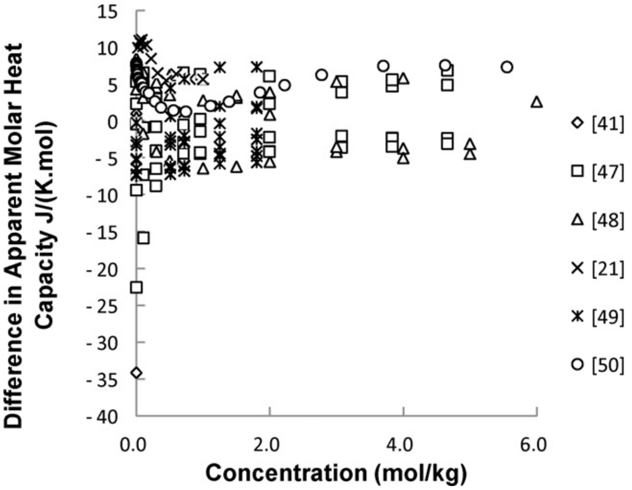

Fig. 2. KCl(aq) deviations of apparent molar heat capacity data from the Pitzer model.

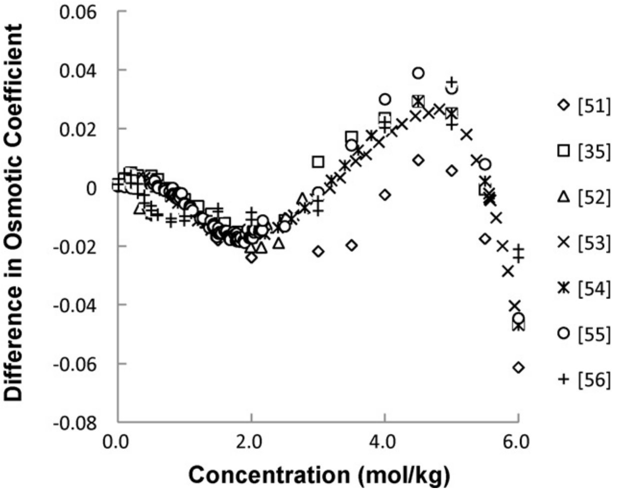

Fig. 3. $CaCl_2$(aq) deviations of osmotic coefficient data from the Pitzer model.

7. Case study 3

Fig. 3 shows the deviations of experimental data from the physicochemical optimiser model for aqueous calcium chloride, $CaCl_2$(aq). The range of data extracted from the database was chosen as 25–100 °C, 0–6 m and 1 bar, yielding a total of 523 osmotic and activity coefficient points [35,51–56]. The osmotic coefficient data are seen to cycle about the Pitzer model at all temperatures.

These large cyclic systematic deviations have been observed previously: in their study of this system, Rard and Clegg [57] improved the agreement with the experimental results at 25 °C by modelling the $CaCl^+$ species present in solution along with calcium and chloride ions. The coupling of thermodynamic models for strong electrolyte solutions with those which exhibit significant chemical speciation as represented in the JESS speciation database will be the subject of our future investigation and development.

8. Concluding remarks

The aim of this work is to represent the targeted physicochemical properties in a thermodynamically-consistent way as accurately as possible *from the information currently available in the literature*. Whilst the automatic process outlined here approaches this problem in much the same way as happens when (human) experts review, assemble and assess primary experimental measurements to develop the highest quality reference data, the two processes have different objectives and should not be confused. Our automated process strives to achieve a thermodynamic *simulation* capability which can be used with confidence over a given range of conditions to obtain a fair representation of chemical system behaviour as it has so far been described. In addition to the primary data, JESS thus depends heavily on critical compilations by the relevant experts. *JESS cannot perform their job and it does not try to do so*.

The software described in this paper has a different role. Its mission, in addition to recording and using the best available reference data, is to facilitate the making of general, rapidly-developed, easy-to-use, up-to-date and reliable models for aqueous chemical systems. This means:

- accommodating the inter-dependence of many 'primary' experimental results as published, which is pervasive but difficult to untangle;
- dampening the chaotic variations which occur when one widely-used, critically-determined thermodynamic parameter set is superseded by another; and
- enabling modellers quickly to inspect the relevant data in the literature whenever this is needed to judge the robustness of their results, including most crucially rapid comparisons with the latest available corresponding reference values.

Our experience makes clear one thing above all – even the most authoritative reference data set is ephemeral [58]. It is wrong to think that modellers only need today's best evaluation of any given thermodynamic system. This is not only because critical reviews can never be perfect but also because they are always fixed in time and they are always limited in their scope. Aside from instrument calibration purposes, which is a very specialised use, thermodynamic models generally have a wide reach, which raises issues of coping with enormous amounts of diverse data, of consistency between chemical system parameters *over time* and of extrapolations beyond the range of measured conditions (especially extrapolations into multicomponent space). It is to address these issues that thermodynamically-consistent models are constructed automatically by JESS programs.

The JESS suite of executable programs and databases is made available for academic (non-commercial) purposes at nominal cost. See http:\\jess.murdoch.edu.au for details.

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