

**Progress in aqueous solution modelling: Better data and better interfaces**

Darren Rowland<sup>1,2,\*</sup> and Peter M. May<sup>2</sup>

<sup>1</sup> Fluid Science and Resources Division, University of Western Australia, Crawley 6009, Australia

<sup>2</sup> Chemistry, Murdoch University, Murdoch 6150, Australia

\* Corresponding author. Tel: +61 8 6488 8653

Email: Darren.Rowland@uwa.edu.au

Email: P.May@murdoch.edu.au

## **Abstract**

The Joint Expert Speciation System (JESS)

thermodynamic information about aqueous electrolyte solutions. Comprehensive and up-to-date thermodynamic models undoubtedly require large databases but size alone, without well-designed data structures and good data assessment procedures, is insufficient. Computer databases are not like tables in a book; they should be constantly evolving, easy to search and specifically designed for processing by large-scale, automated facilities, including tests for careless errors and internal consistency. T

more relevant than ever: without expert analysis and critical judgement, limitless storage capacity and computational power are likely just to add confusion rather than achieve meaningful insights into chemical problems.

Several examples are provided to demonstrate the application of new methodologies to problems of differing size and complexity including harmonisation of aqueous reaction equilibrium constants for more than 50,000 chemical species, systematic critical assessment of the thermophysical properties of aqueous glycine and its solid-liquid equilibria over wide ranges of temperature and pressure, and development of standalone programs for users lacking training in chemical speciation problems. Extension of these methods to new applications is discussed.

## **Keywords**

Aqueous electrolyte; Chemical speciation; Physicochemical properties; Solubility; Thermodynamics

## **Introduction**

In thermodynamic calculations for aqueous solutions, the multi-factorial nature of the errors involved makes them particularly difficult to identify and control [1, 2]. The multi-dimensional space of conditions over which such errors operate, coupled with serious ongoing theoretical inadequacies [3], makes their impact even more difficult to quantify. These issues are further exacerbated by numerical regression of experimental data using empirical functions with too many adjus

much more likely than they may initially seem, as has occurred recently with tin [12, p. v], iron [5, p. vi and p. 109] and sulfur [13].

While the whole suite of benefits which can reasonably be expected from the application of artificial intelligence to these various tasks remains admittedly distant, considerable progress has been made in recent years, as a result of which better data and better computer interfaces are steadily becoming available. The keys to these developments are wider recognition of the challenges involved plus broad and careful design of the data structures, algorithms and code required to address them. Only in this way can we possibly cope with the magnitude of data which confronts us as well as, hopefully, maximising the dividends offered by modern computing power. We must keep up-to-date more efficiently, reduce the frequency of errors more effectively, and improve the reliability of thermodynamic models more generally. These are the guiding ambitions which have underpinned the development of our Joint Expert Speciation System (JESS) software package for over thirty years [14] and which are now progressively coming to full fruition.

## JESS databases

It takes significant time investment to collate experimental measurements and other information from the literature. The collation of data for JESS databases has resulted in a significant body of assessed data (Table 1) but these data are difficult to utilise properly unless they are stored comprehensively, kept up-to-date and regularly processed to ensure thermodynamic consistency. Given the scale of this task, it can only be achieved by automated tools/expert systems to help with data assessment and to manage the required numerous and sometimes complicated numerical manipulations.

**Table 1.** Summary statistics related to JESS databases.

<i>Thermodynamic database (JPD)</i>	
• Number of records	278,137
• Number of reactions	80,492
<i>Physicochemical property database (FIZ)</i>	
• Number of records	510,366
• Number of solutes	860
<i>Solubility database (SOL)</i>	
• Number of records	125,657
• Number of non-aqueous phases	2,228

### *Thermodynamic database*

The JESS Thermodynamic database interface (JTH) [15] is employed to store and manipulate thermodynamic data including equilibrium constants, changes in Gibbs free energy or enthalpy, and electrochemical potentials. It is used in particular to manage the JESS Parent Database (JPD) which holds the current version of all the reaction data we have so far compiled from the literature. Currently, the database contains over 80,000 reactions and over 226,000 equilibrium

constants spanning interactions in solution of some 100 metal ions with more than 2,500 ligands.

Many features of JTH were designed to overcome problems affecting other databases of equilibrium constants. While such databases typically restrict the types of allowed reactions or species that can be represented, reactions in JTH may be written in any form subject only to mass and charge conservation. This allows all types of reactions (formation, step-wise, overall, redox, etc.) to be expressed and processed. Unlike other major compilations of equilibrium constants, ternary complex formation is handled naturally by the same reaction-processing conventions as all other reactions: this has allowed JTH to become the largest single source of

usually stored exactly as they appear in the literature which minimises errors and facilitates checking of values. Subsequent manipulations of the data such as to eliminate duplication, achieve thermodynamic consistency, regress parameters, or to conform to a particular set of basis species for speciation modelling are performed as needed. These facilities are in contrast to those of other chemical speciation modelling facilities.

Even the storage of more than one equilibrium constant value for any reaction at given temperature is expressly forbidden in most thermodynamic databases. A major limitation then is that it becomes unclear to users whether the values in the database are the best currently available or just the best that were available to the database compilers at the time. As databases inevitably age and new data appear in the literature, the latter situation becomes ever more worrying. A distinguishing feature of JTH is that it is constructed to allow large (practically unlimited) numbers of data for each reaction even under identical conditions. In this way JTH functions as a repository for permanent storage of thermodynamic data so users can always be clear about which data from the literature were known to the compilers at the time when the database was last modified. Some of the most important advantages of taking such a comprehensive approach to data storage are that data from independent sources can be compared readily, the status of literature knowledge and reasons for preferring particular data can be made explicit, and data in multiple background media can be recorded. The latter is in contrast to the NIST database for stability constants of metal complexes [16] and is especially beneficial because equilibrium constants matching the background medium of interest as nearly as possible can be extracted from the database for use in particular chemical speciation calculations.

In addition to storing the identity of the background electrolyte, the temperature and ionic strength, and information about the literature reference, every thermodynamic datum is also assigned an estimate of its reliability; this allows the database to be both comprehensive and critical. JESS is very much concerned with the quality of the thermodynamic data used for equilibrium modelling. Every thermodynamic parameter entered into JTH is associated with a weight indicating how reliable the parameter is assessed to be. These weights are imposed in the automated fitting procedures to determine parameters for well-proven thermodynamic equations (e.g. [17]). The fits can then be used to identify outlying data and achieve consistency internal to the reaction data. More advanced techniques such as those described in JESS Part VI [18] are finally employed to achieve consistency across all reactions in the database. A relative combined weight from linear combinations of reactions is used to select the best

thermodynamic parameters relevant to a given speciation calculation. For example, the more reliable reactions are retained when redundancies are detected and eliminated. The outcomes of these assessments are also fully traceable to the original experimental data.

### *Thermophysical property database*

The JESS Physicochemical Property Database (FIZ) stores information related to the physicochemical properties of aqueous strong electrolyte solutions including activity coefficients, water activity, enthalpy of dilution, apparent molar isobaric heat capacity, density difference relative to water, and many others. The system recognises 45 common cations, 45 common anions and up to 35 non-electrolyte substances. Most of the data refer to well-defined solutions containing one or two simple electrolytes such as NaCl(aq), KOH(aq) or  $\{(1-z)\text{HCl} + z\text{MgCl}_2\}$ (aq). In practical terms, the eventual size of the database is essentially unlimited meaning that the physicochemical property database can act as a comprehensive repository of all relevant information. The total number of physicochemical data values recorded in FIZ now exceeds 510,000.

To allow literature data to be represented as closely as practical to its published form, the physicochemical database has flexible conventions for data entry: a variety of common units are recognised including for pressure (e.g. bar, atm, torr, MPa), temperature (C, K, F) and different volumetric and gravimetric concentration scales (e.g. molality, molarity, mass fraction, g/L). Mixtures are accommodated in a similar way to pure solutions by specifying each concentration independently or by specifying the total ionic strength and the ionic-strength fraction of either component (the fraction of the other being determined by difference). For rare cases where the above mechanisms are not sufficient for data to be entered as they appear in the literature – usually due to the use of obscure units – further flexibility is provided by interpreting and implementing algebraic functions that modify the published values and convert them to more convenient forms. Here too, this automatic approach to data storage minimises errors and facilitates checking of the data.

As with the JESS thermodynamic database weights are assigned to all data in the physicochemical database. Initially the effort put into weighting is kept to a minimum and only particularly prominent factors that should obviously (and significantly) decrease or increase the weight away from a typical default value are considered. We carefully avoid elevating limited sets of data (indeed, often very limited sets) to become 'the best' available, no matter how reputable the authors. Undue influence given to single studies that have not been confirmed by other investigators (the so- is often later exposed by subsequent data measurements and/or authoritative critical assessments. That all experimental measurements are subject to error is overlooked too often; such errors are often systematic and undetectable except by comparison with truly independent observations [19].

Several methods of analysis are available for evaluating the consistency of datasets and determining appropriate weights. Plotting the data is, of course, an immediate and basic method for revealing gross outliers and whether or not the data adhere to expected physical behaviours such as the Debye-Huckel limiting law, structure-breaking/structure-making temperature

phenomena, or that density increases with increasing pressure [10, 20]. Unlike other databases the JESS physicochemical database contains published properties derived from primary data: for example, when both density and apparent molar volume are reported they are both stored in the database; this

typographical and other possible errors. The benefits from this approach sometimes go even further – a recent example involving lithium tetraborate highlights that invalid model results and conclusions are obtained when based on flawed conversion from primary data [10]. In addition to data visualisation, which is readily applicable to binary mixtures but becomes difficult for ternary mixtures, fitting the data to standard equations also helps to check the reliability of the data and the appropriateness of the weighting. For physicochemical properties several options are available and implemented in JESS including Pitzer equations [19, 21], Hückel equations [22], linear mixing rules such as Zdanovskii, Harned or Young [23–25] and other equations such as Redlich-Meyer. As complete literature information is linked to all data the results of these model fits are fully traceable.

A particularly valuable recent finding is that the physicochemical properties of strong aqueous electrolytes are in general equally well fitted by both the Pitzer and the Hückel equations, with only relatively small differences appearing between these fits *when good data are being regressed*. In other words, deviations between the two functions tend to arise mostly as a result of errors in the data rather than from inaccuracies attributable to the models themselves. Evidently, the errors are propagated differently whereas good data and the predictions of both fitting functions tend to coincide.

Once any dataset has been subjected to an appropriate analysis like equation fitting, visualisation or quantitative comparison with other datasets, it becomes easier to determine the agreement with independent and reputable observers (should other datasets exist). As new datasets appear in the literature, or new insights are gained into the fundamental behaviour of such electrolyte solutions, re-assessment of existing weights is routinely necessary. Thus, the weights in JESS are not forever fixed but rather should be expected to change over time as the available data and their assessment progressively improves. The importance of automated and systematic data handling methods (including algorithms for equation fitting) is especially evident if this fitting process is to be practical, reproducible upon demand, and traceable to the underlying literature data. Good design of the database is seminal to this effectiveness.

### *Solubility database*

The key distinguishing factor of the JESS Solubility Database (SOL) is that it is capable of handling physicochemical data associated with chemically reactive systems, especially those where non-aqueous phase(s) exist in equilibrium – either thermodynamic or metastable – with an aqueous solution. The key idea is to store literature data in as general a way as possible and to have a variety of computational mechanisms for finding, validating and representing such data. Great flexibility is thereby achieved for any chemical system whose composition can be specified in terms of the 60,000 species recognised in JPD.

On each record the SOL database stores the conditions of pressure, temperature and composition under which solubility and other specified, measurable properties of aqueous solutions have been quantified. The solution density can also be supplied to facilitate the conversion between gravimetric and volumetric concentration scales. If known, measured pH, Eh, gaseous species partial pressure, and other quantities may be similarly provided. As with other JESS databases an assessed weight for the dataset is required; initial effort spent on setting the weight is minimised by focussing on the most important factors indicating data reliability (for example, the attainment of thermodynamic equilibrium versus evaporation [26]). Subsequent refinement of the weights is usually conducted after visual inspection, regression by suitable equations, and comparison with other literature values.

To follow the usual path taken with other JESS databases, where data are stored in a form as close as possible to the original in the literature, a wide variety of pressure, temperature, concentration, and physical property units are recognised and automatically interconverted by standard algorithms. Similarly, algebraic functions can be specified and detailed literature information can be recorded. Each dataset is given a descriptor to help identify and find relevant systems. For solubility records, the chemical identity of the solid or gaseous phase in equilibrium with the solution is given either in terms of its full symbol as in the thermodynamic database or as an abbreviation. This flexibility once again helps with checking the data and minimising errors related to data entry.

Storing large numbers of solubility data requires a compact, and ultimately machine-processable, format which completely describes data for potentially complicated chemical solutions. Existing databases (e.g. Ref. [6]) often omit key information relating to the operative chemical reactions. Where pressure, temperature, composition and concentration of solution, measured property values, allowed chemical reactions or identities of solid phases are missing in SOL, the dataset is earmarked as unfit for regression purposes.

Although SOL is still in an early stage of development and its coverage of the relevant literature remains modest (Table 1), the usefulness of SOL has already been demonstrated in a recent critical review and equation of state development for aqueous glycine [27]. As part of that work, widespread property values for glycine(aq) including solubility, isopiestic data, density and heat capacity were captured and stored. After extensive analysis involving visualisation, interconversion of related properties such as osmotic coefficients and water activity, and model fitting, an equation of state based on the Pitzer equations was developed by regressing more than 2,500 data points. It is worthwhile noting that in this study more than 1,200 literature data were found to be unreliable and so had to be excluded from the regression. (These rejected data are nevertheless maintained in SOL with zero weight for the reasons given above.) This comprehensive collection of critically-assessed data and traceable models has established the efficiency and effectiveness of this recently-developed JESS database.

## **JESS interfaces**

Computer interfaces for chemical applications tend naturally to be complicated by the nature and diversity of chemical reactions. Matters are made worse when software vendors try to



provide all things to all users and, relatedly, when they introduce incremental new design/bolt-on features. Learning how to use these complicated interfaces is a burden on the user but one that may have to be accepted because there is no other software to do the job any better. Due to its long history [14] JESS has a large number of Windows MSDOS command-line tools for database interaction, performing speciation calculations and other tasks such as critical data assessment, physicochemical property prediction and data manipulation/transmission. Although such tools are powerful and highly efficient, they require expertise which takes time to learn. Accordingly, a number of more user-friendly tools with graphical interfaces have also been developed recently for accomplishing certain common calculations. These simple interfaces are much easier for any user to operate.

The new JESS interfaces take advantage of several modern computer languages such as Visual Basic for Applications (VBA, typically as part of Microsoft Excel), python, and HTML for development of web-based utilities. Nowadays, these other languages are fully capable of interacting with the FORTRAN-based codes which comprise the majority of JESS code. Our experiences with developing interfaces in each of these languages/frameworks are described below. With these interfaces in general our intention is to present: (i) all available options on a single screen and (ii) sensible defaults so that the user can quickly learn how to get something comprehensible and representative of the kind of output to expect. This approach helps particularly with input syntax,  $\text{Na}^{+1}/\text{Cl}^{-1}$  - the JESS symbol for NaCl(aq) - because the way forward is made more obvious by a specific example.

#### *VBA (Microsoft Excel)*

One of the main reasons for making an interface through VBA is that most computer users with scientific training will already be familiar with Excel and its major functions (such as sorting and plotting datasets). Although Excel itself is often used as a data repository by users it is not well-suited to that purpose; the JESS databases described above have much superior features. On the other hand, when it comes to visualising data it is very convenient to compile the FORTRAN code into a Dynamic Link Library (DLL) and call the DLL from Excel using the in-built VBA programming facilities.

Excel has straightforward facilities for developing customised user interfaces. The Excel-based interface used most often has a distinctive Toolbar icon. The main plotting data from the JESS thermodynamic, physicochemical and solubility databases (Fig. 1).

**Fig. 1** - n Microsoft Excel UserForm object for extracting and plotting data for different electrolyte solutes, physicochemical properties and experimental conditions. Property models including the equations of Pitzer and Huckel can be enabled.

As the DLL contains JESS code for optimising parameters in the equations of Pitzer, Huckel and Redlich-Meyer to describe properties such as activity and osmotic coefficients, relative molar enthalpies, apparent molar heat capacities and apparent molar volumes, the 8-ball facility has proven itself to be an especially powerful tool in our critical assessment of data from the literature. On start-up, users can plot the data for the activity coefficients of NaCl(aq) at 25 °C with the click of one button (which aims to reduce the learning curve for new users). Other electrolytes and physicochemical properties can then be selected by modifying text-fields. The automated regression procedures for common thermodynamic modelling frameworks can be turned on or off by clicking the appropriate checkbox. As results from the databases and model regressions appear in Excel near-instantaneously, we have found that 8-ball provides us with an effective mechanism for visualising physicochemical property trends between different electrolytes.

### *Python*

The main reason to develop an interface using python is that standalone programs for specific applications can be produced very conveniently. An advantage of creating a standalone

program is that all extraneous details otherwise faced by users can be avoided and the focus placed just on solving a particular problem. We have chosen to use python although it is not the only language which supports standalone graphical programs. This choice was made because python has become a particularly popular tool in the scientific community for interacting with FORTRAN and because it has many well-tested libraries with useful functionality. An example of interfacing between FORTRAN and python is given in the Supporting Information.

The major use of python in JESS has been to develop user-friendly interfaces for speciation calculations. New users to JESS can face a steep learning curve if this is their first introduction to a generalised speciation solver (capable of handling thousands of species at a time): by building an interface in python a small discrete number of species can be presented to the user and most of the decisions that require experience and expertise to make can be handled behind the scenes. This approach to speciation calculations does not, of course, suit every speciation problem but it works well when the interactions between major species have been well-characterised experimentally and the range of possible overall compositions is well defined.

### *HTML*

Unlike the other tools mentioned above, the JESS web-based interface allows users from all over the world to access certain materials without the need to install any software except a web-browser. The JESS website (at <http://jess.murdoch.edu.au>) thus provides (i) access to our databases, (ii) facilities to calculate results from various published models, and (iii) graphical representation of certain datasets and model predictions based on data from the literature. The thermodynamic reaction database (JPD) is open to global inspection, allowing equilibrium constants from the chemical literature for more than 80,000 reactions to be viewed and searched in their entirety. Tools for calculating physicochemical property values for various aqueous strong electrolytes based on Pitzer and Huckel equations are also available [20, 22, 28], as are the results from the recently published equation of state for glycine(aq) [27]. It provides convenient links to JESS publications, other documentation, help pages, literature details, and so forth.

These web-based tools rely on standard HTML input and output mechanisms that users will be familiar with, ensuring that the system is readily approachable and straightforward to use.

The website facilities developed as part of JESS take advantage of the fact that our FORTRAN codebase compiles under various computer operating systems. Certain programs have been developed that when compiled for our Linux-based web server can be run after being called by a lightweight set of perl instructions; the JESS programs output HTML code directly for presentation on the website, including javascript code that provides plotting capabilities for data visualisation.

### **Future work**

In addition to the many challenges currently facing thermodynamic modellers [3], database compilers face unique hurdles related to keeping up-to-date with the ever-growing number of published experimental data. This is an area where solution chemists globally could profit greatly from increased cooperation or partnership between respected organisations such as IUPAC, NIST and NEA.

A number of benefits of automated methods in JESS for critical data assessment have been described above but codifying expert knowledge into practical and robust algorithms remains an ongoing task that requires deep understanding of the features and limitations of both the types of experimental data typically encountered and the models that are used to correlate and predict those data. When fitting model parameters to experimental data the properties of the data (such as uncertainty, range, gaps, systematic error) and choice of data to include/exclude can make substantive differences to the final model result. How to equip researchers with improved software tools for understanding these dilemmas and making appropriate choices will be subject to future investigation.

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