

# Database of Chemical Reactions Designed To Achieve Thermodynamic Consistency Automatically<sup>†</sup>

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The development of a large database, and associated computer software, for thermodynamic parameters of chemical reactions in aqueous solution is described. The aim has been to tackle some of the uncertainties that currently restrict the chemical modeling of aqueous, multicomponent mixtures. A computer package is now available that can be informed progressively of new experimental data, critical data evaluations, and established chemical trends so that sound and up-to-date thermodynamic calculations can be quickly and conveniently performed. This has been accomplished by storing a large amount of (inherently inconsistent) chemical data from the literature and, from this, producing a consistent set of mass balance equations by automatic means. The basis of the chemical and numerical judgments made during this process is briefly outlined. The criteria for selection of the best thermodynamic values and of the best linear combinations of reactions are given particular attention.

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## Introduction

Serious discrepancies between published thermodynamic parameters of chemical reactions are well-known (e.g. refs 1–5). Since there are many different causes of these problems (such as experimental error, inadequate theory, and carelessness), they can be very difficult to pinpoint and to eliminate. The situation is made worse because many thermodynamic data persisting in the scientific literature stem from values that are later corrected or become experimentally superseded.

In this regard, a great effort is needed for critical assessment of all the relevant primary measurements and for their transformation into thermodynamically consistent datasets. Such work not only demands considerable expertise and dedication but is also liable soon to be outdated as new measurements are made. This means only few of the many tens of thousands of chemical reactions of interest have been adequately characterized. Chemical modeling is thus often compromised. Figure 1 summarizes reasons why we believe this unsatisfactory situation persists.

To address these issues, we have developed a suite of computer programs that build and maintain a database of chemical reactions and their thermodynamic parameter values.<sup>6,7</sup> The resulting JESS (Joint Expert Speciation System) database now contains over 216 000 thermodynamic constants associated with more than 72 000 chemical reactions. It can be inspected on the worldwide Web at <http://jess.murdoch.edu.au/>.

A key attribute of this database is that any form of chemical reaction can be handled, for example, all the common types of solution equilibria including protonation, complex formation (binary and ternary), redox reaction, solubility (of solids, liquids, or gases), and adsorption.

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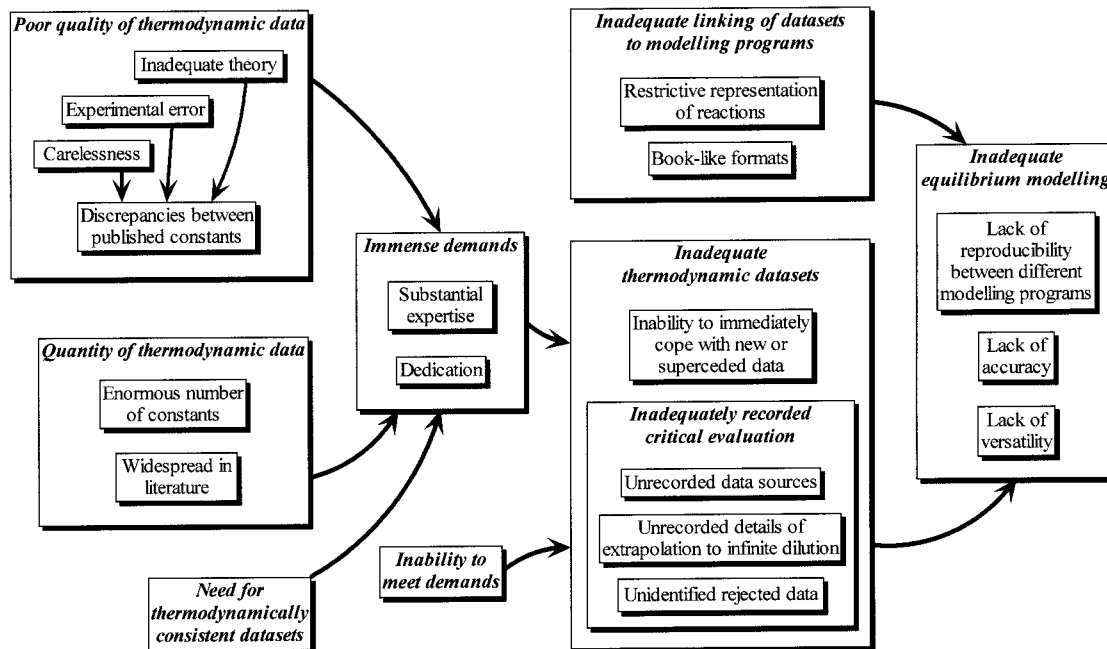
Examples of the formats used for various reactions are shown in Figure 2. These formats allow each reaction to be checked for charge and mass balance, and critically, they permit linear combination of reactions.

For each reaction, a practically unlimited number of associated thermodynamic values can be stored. (The largest number needed for a single reaction so far is 581, but this could easily be increased by one order of magnitude, or probably even two.) These reaction parameters can be equilibrium constants, Gibbs energies, enthalpies, entropies, heat capacities, or standard electrochemical potentials. Each such value is individually associated with (i) the conditions under which it was measured, that is, the identity of any background electrolyte, the temperature, the pressure, and the ionic strength, (ii) the reported uncertainty, (iii) the literature reference, (iv) an optional comment, and (v) our current estimation of its reliability, on a weighting scale of 0–9. The general appearance of these data, for a typical reaction, can be seen in Figure 3.

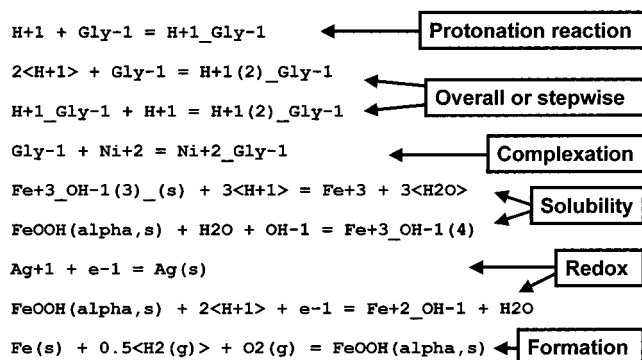
This paper describes how these data are now being manipulated automatically and why this is necessary. The principal aims are to achieve thermodynamic consistency while simultaneously eliminating redundant reactions from equilibrium calculations. This has required the encoding of procedures to select data for quality and for relevance of experimental conditions as well as to establish the most appropriate linear combinations of reactions.

## Justification

Achieving thermodynamic consistency is combinatorial in nature and, hence, can become prohibitive with large, multicomponent systems. Thorough (manual) evaluations are accordingly confined to small chemical assemblages (e.g. ref 8) or can only be performed infrequently, as in the case of the more extensive NBS/NIST-sponsored projects (e.g. ref 9). A computational procedure that automatically achieves thermodynamic consistency would evidently be of great assistance in terms of including the latest data, reducing the burden of mundane work, and minimizing errors. However, there are several other important, and



**Figure 1.** Problems with equilibrium modeling—reasons for the status quo.



**Figure 2.** Representative JESS reaction formats.

perhaps more interesting, issues which can also be tackled by a chemically intelligent computer system in this area. Two different kinds of problems, in particular, need to be overcome.

First, none of the other major compilations of equilibrium data for chemical speciation calculations<sup>10–14</sup> can be processed automatically. This is largely because they exist in a booklike format, be they electronic<sup>10,11</sup> or on paper,<sup>12–14</sup> in which the reaction definition has not been recorded appropriately for numerical processing purposes. It is also because aqueous equilibrium data are often classified in terms of “metals” and “ligands”, that is, according to a predetermined set of basis species, which involves implicit assumptions about kinetic constraints.<sup>15</sup>

To avoid these limitations, an entirely general method of representing chemical reactions on the computer is necessary and has been developed, as outlined above. Given the wide diversity of possible chemical relationships, it is important that there be no restriction of chemical reactions, or of the chemical species involved in them; otherwise, much available thermodynamic information can be lost. For example, neither the IUPAC<sup>10</sup> nor the NIST<sup>11</sup> electronic databases, which are the two largest individual collections of equilibrium constants, can ever be comprehensive, even for quite simple chemical systems, because they are not specifically designed to deal with the stoichiometry of

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Reaction No. 6,453
Gly-1 + Ni+2 = Ni+2_Gly-1

>>> Last modified: 21-Dec-99 20:45

1 t=10 I=0 Inf. Dilution      lgK 6.28(0.01SD) Wgt=4 EDH[2491]
2 t=15 I=0.2 KCl              lgK 6.04(3SF) Wgt=4 MGL[999]
3 t=20 I=0.01 Unknown        lgK 6.1(2SF) Wgt=0 MGL[999]
4 t=20 I=0.1 KCl             lgK 5.73(3SF) Wgt=6 MGL[2057]
5 t=20 I=0.1 NaNO3          lgK 5.8(0.05SD) Wgt=6 MGL[2036]
6 t=20 I=0.5 KNO3           lgK 5.77(3SF) Wgt=5 MGL[999]

21 t=25 I=0 Many Media      lgK 6.16(0.02SD) Wgt=8 EIU[1555]
22 t=25 I=0.05 Me4NNO3      lgK 5.850(0.002SD) Wgt=6 MGL[5829]

51 t=25 I=1 NaCl             lgK 5.63(0.01SD) Wgt=8 CRV[2796]
52 t=25 I=1 NaClO4          lgK 5.69(0.03MD) Wgt=5 MGL[999]

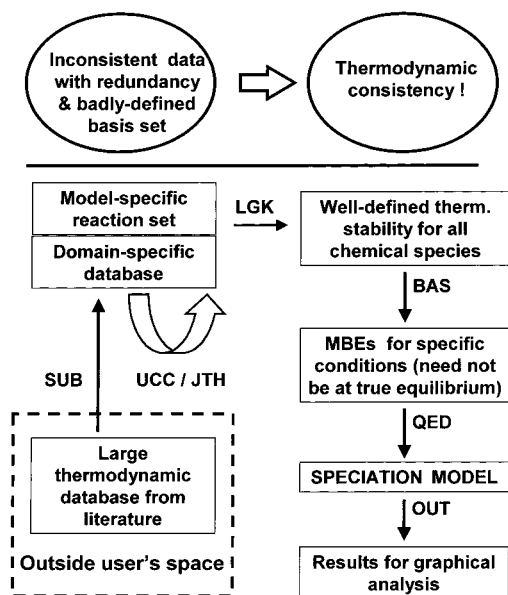
75 t=25 I=1 KNO3             dH -20.3(3SF)kJ Wgt=5 CRV[552]
76 t=25 I=3 LiClO4          dH -6.52(3SF) Wgt=5 MCL[7202]

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**Figure 3.** Data for a typical reaction. Equilibrium constants (lgK) and enthalpies (dH) at various temperatures (t) and ionic strengths (I) and in different electrolyte media; reported errors are shown in terms of significant figures (SF), standard deviations (SD), or maximum deviations (MD); the literature reference for each datum is given as a number in square brackets, corresponding to the entry in the literature database; also included for each datum is a weighting factor (Wgt) as described in the text and a technique code where, for example, MGL = measured by glass electrode, MCL = measured calorimetrically, EDH = estimated by Debye–Hückel extrapolation, EIU = IUPAC estimate, and CRV = value from a critical review.

standard formation reactions, ternary complex formation, or ligand–ligand interactions.

The second type of problem concerns computer modeling packages that have, hitherto, performed chemical speciation calculations using their own thermodynamic databases. Such databases, unfortunately, contain only a very small fraction of the available data (compared to the sources discussed above). However, of even greater concern, is the manner in which their thermodynamic data have been stored. Several fundamental issues, which are further addressed below, include (a) the storage of standard state values without the corresponding extrapolation functions and parameters used in their derivation, (b) the use of Gibbs energies of formation rather than the equilibrium



**Figure 4.** Sequence of operations used to attain thermodynamic consistency automatically. The model's data are extracted from the JESS Parent Database (SUB stage), assessed as described in the text to yield the best possible values of the thermodynamic parameters (UCCs) for all species (LGK stage), transformed into a consistent set of mass balance equations that are expressed in terms of the basis species concentrations deemed most appropriate (BAS stage), solved for particular conditions (QED stage), and prepared so that the results can be displayed in various ways (OUT stage).

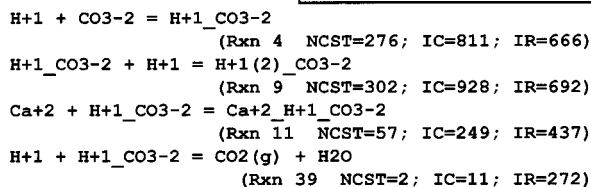
constants, or Gibbs energies, of the most appropriate reactions, (c) the predetermined, and hence invariant, choice of species whose concentrations or activities are treated as unknown (the so-called master or basis species), and (d) the failure to record properly why particular literature values have been selected in preference to others and the full consequences of these decisions.

The collective outcome of all these deficiencies has been to undermine the reliability of chemical equilibrium calculations to a considerable, and often surprising, extent. The striking differences in speciation distributions obtained by independent experts in a double-blind study commissioned by the European Nuclear Energy Agency were one of the major motivations for early JESS development.<sup>6</sup> There are still surprisingly large changes over time, both of the modeling predictions themselves (e.g. ref 16) and of the critically assessed thermodynamic parameters on which such models are based (e.g. ref 12). There is little evidence to suggest that such changes are universally diminishing in magnitude as chemical systems become better characterized; on the contrary, the results of periodic critical evaluations of large systems of thermodynamic data, such as occurred in the CHEMVAL project,<sup>17</sup> are often seemingly chaotic in nature (e.g. Tables 3 and 4 in ref 18 and Figures 6 and 8 in ref 19). It can take many years before even gross errors in modeling databases are detected (e.g. refs 1 and 3). All this suggests that the root of the problem may be associated less with the arrival of new experimental values than it is with the way thermodynamic data are currently being processed.

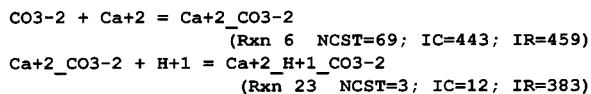
### Strategies

In our view, understanding the problems described above and, hence, finding a better way forward hinges on a single proposition: full automation is essential to manipulate

#### Reactions involving H+1\_CO3-2



#### Reactions involving Ca+2\_CO3-2



**Figure 5.** Snapshot of typical results from the LGK stage shown in Figure 4. The abbreviations used are defined in the text.

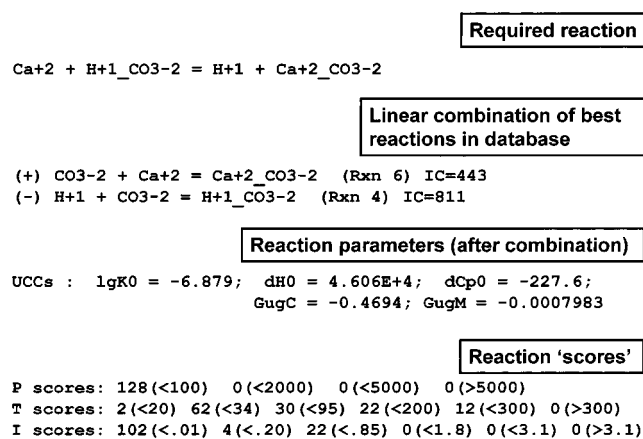
properly the sizable and intricate datasets involved in modeling most aqueous chemical systems outside of the laboratory. This means bridging the gap between the large, booklike databases of IUPAC<sup>10</sup> and NIST<sup>11</sup> and the small, processable databases associated with modeling packages such as EQ3/6, PHREEQE, MINTEQA2, and SUPCRT92 (e.g. refs 20–23) that are currently being employed for most speciation modeling purposes.

Two important aspects of the scheme are (a) to make explicit the critical judgments and assumptions involved in selecting the thermodynamic data and (b) thereafter to achieve thermodynamic consistency by a fully automatic algorithm. In this way, the many decisions that always determine the results of large equilibrium models can be scrutinized and refined, so that hopefully outcomes will converge over time.

At present, it is practically impossible to trace all the thermodynamic parameters stored in large modeling databases back to their origin in the chemical literature.<sup>24</sup> Just as bad, comprehensive records of those data that have been rejected in the critical evaluation process are rarely, if ever, available. To combat this problem, we generally store in the database all values that we locate in the literature but flag those considered “worthless” to preclude their use, and we note reasons for the decision alongside rejected values. We also record all data in a form as close as possible to that of the original literature source, so as to minimize transposition errors and to facilitate checking. This can be done because of the general way in which our reactions can be written and because redundant reactions are avoided automatically at a later stage.

One of the worst aspects of many thermodynamic compilations and databases for aqueous systems is the omission of details about the theoretical function(s), and parameters, adopted in the extrapolation to obtain infinite dilution (standard state) values. The contents of these databases thus tend to be regarded simplistically as “right” or “wrong”, overlooking the complicated interplay between them and the chemical postulates imbedded in any model, which together actually determine the models’ quantitative predictions. It is of course only the correctness of these predictions that counts, but all too often, this is untested or achieved by parametrization.

It is not surprising that predictions fail when different functions or parameters are subsequently used with stored standard state values to back-calculate the chemical behavior of real solutions. Discrepancies arising in this way are, nonetheless, often just attributed to inadequacies in the theory of activity coefficient change! The obvious remedy is to ensure that the chemical information obtained



**Figure 6.** Snapshot of typical results from the BAS stage shown in Figure 4. The abbreviations used refer to the unconditional correction coefficients or UCCs in which  $\lg K0$ ,  $dH0$ , and  $Cp0$  are the reaction's equilibrium constant, enthalpy change, and heat capacity change, respectively, under standard state conditions at 25 °C and  $\text{GugC}$  and  $\text{GugM}$  are the semiempirical parameters for the activity coefficient effect of ionic strength and temperature on the equilibrium constant;<sup>23</sup> the "scores" attempt to quantify the suitability of the selected linear combination of reactions with respect to the pressure (P), temperature (T), and ionic strength (I).

experimentally is preserved in a complete and self-consistent way. This occurs, for instance, with sets of properly determined Pitzer<sup>25</sup> or HKF<sup>23</sup> coefficients. Our function is an extended version<sup>26</sup> of the Density model.<sup>27</sup> It has recently been shown to calculate satisfactorily the conditional equilibrium constants (often referred to as concentration quotients) in aqueous solutions to high temperature (<250 °C) and ionic strength (<5 M).<sup>26</sup> This function has the advantage that it minimizes the number of regressed parameters and, hence, we feel, should improve and generalize our predictive capability.

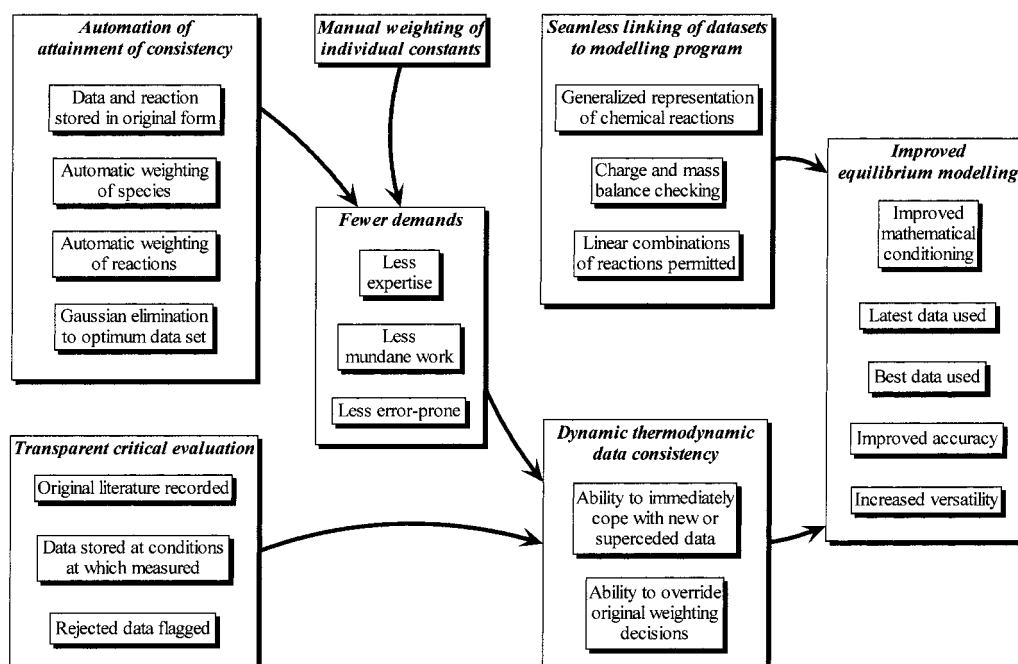
### Automatic Data Selection

Given that the chemical reactions, as stored in our database, can be manipulated algebraically, the mechanics

by which thermodynamic consistency is achieved are straightforward. The steps are shown in Figure 4. All reactions of possible relevance to the model (as defined, for example, by the chemical elements in the system) are first extracted from the database; they are then converted, by a process of Gaussian elimination, into the consistent set of relationships that define the thermodynamic stability of all chemical species in terms of a basis set. These relationships appear as the linear combinations of reactions in the database that must be used to calculate the concentrations of species at equilibrium. This is done using parameters of the extended Density model,<sup>26</sup> called "unconditional correction coefficients" (UCCs), these being periodically predetermined for each reaction by regression of the raw values held in the database. The UCCs are simply multiplied by the appropriate reaction coefficient (in the linear combination) and summed. Mass balance and other equations can then be constructed in the usual way and solved for any specified set of conditions.

A sequence of JESS computer programs is used to accomplish these tasks. Some outcomes of the way the data are manipulated (by the steps shown in Figure 4) are illustrated in Figures 5 and 6. In this way, chemical equilibrium calculations can be set up and performed easily and quickly. Although an upper limit is not well defined in the code, the system can cope with models involving at least 10 000 chemical species.

The success of this approach toward data selection is determined by the Gaussian elimination procedure. For the most part, this depends on how well each linear combination of reactions is selected. The optimum outcome is accomplished naturally by the Gaussian elimination, provided that the reactions and species are processed in the correct order. The criteria for establishing this order are, unfortunately, equivocal. Broadly speaking, those reactions that are best characterized should be used first; this ensures that, if and when reactions are subsequently found to be redundant, those with the least "information content" are the ones discarded. However, the optimum selection of species to be defined by each reaction (or set of reactions) depends on which species are predominant at equilibrium



**Figure 7.** Advantages of automated attainment of consistency.



and, hence, can only be ascertained after the equilibrium calculation has been performed! Luckily, in practice, most equilibrium calculations are not very sensitive to this choice, and in any event, the problem can be solved iteratively if necessary. On the other hand, it is very useful to be able to change the basis set easily: all databases with predetermined basis/master species are prone to difficulties due to mathematical ill-conditioning when the concentrations of these species, as the algebraic unknowns, become too small.

As now implemented in the JESS, the ordering prior to Gaussian elimination is based on “scores” that are assigned to both species and reactions, according to their respective criteria. Species are favored as unknowns (in the ultimate equilibrium calculation) if they are involved in many well-characterized reactions. This is quantified for each reaction (Rxn) by the “intrinsic reliability” factor (IR) shown in Figure 5. Reactions are selected by counting how many of them there are (NCST) and assessing their “information content” (IC). This IC depends both on the proximity of the equilibrium constants’ conditions of measurement (ionic strength and temperature) to those required by the model and on the quality of the data.

Quality is indicated by the “weights” associated with each thermodynamic parameter, as described above. For example, one important criterion is whether there has been only a single value determined for a reaction: multiple values measured independently under the same conditions that agree are given greater weights.

The weights thus provide a key mechanism by which the system is informed of chemical judgments and opinion. They quantify explicitly assessments not only made by us, the compilers of the database, but also appearing in the literature in the form of critical reviews or expert comment. When the weights are modified to reflect a changing view of particular thermodynamic constants, the chemical knowledge embodied in the database evolves. In this way the database may progressively become both comprehensive and critical.

It is important to note that different linear combinations of reactions can be employed for equilibrium calculations at different conditions. For example, an overall formation constant ( $\beta_2$ ) may be preferred over the combination of stepwise constants ( $K_1K_2$ ) when it has been better characterized under the appropriate conditions than the second association constant ( $K_2$ ), and vice versa. Figure 6 shows a very simple example in which two reactions (Rxn 6 and Rxn 4) are combined to yield the required reaction for  $\text{Ca}+2\text{CO}_3-2$ , formulated in terms of the basis species ( $\text{Ca}+2$ ,  $\text{H}+1\text{CO}_3-2$ , and  $\text{H}+1$ ). Although the programmed criteria attach some importance to minimizing the number of reactions in each linear combination, it is quite often the case that five or more reactions in the database must be employed to characterize the thermodynamic stability of certain chemical species. Accumulating errors in the thermodynamic parameters of the combined reactions can then become serious, and if so, they need to be controlled by reformulating the mass balance equations appropriately, that is, by determining a different set of basis species.

## Conclusion

Judgments of data, selection of reactions, and choices concerning the best way to write mass balance equations are always involved in equilibrium modeling and in establishing its thermodynamic input data. There are considerable advantages to automating these procedures, as

encapsulated in Figure 7. It is now possible for all of a model’s primary data to be documented, for opinions to be kept explicit, and for the decision-making process to be codified. This means that equilibrium models can be constructed more transparently, more objectively, and more reproducibly. Accordingly, errors of fact, of judgment, and of procedure can now be detected and corrected more easily. Chemical speciation calculations thus ought to become progressively more reliable.

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