SKI Perspective

Background

Thermodynamic calculations is a fundamental part of the knowledge basis used for assessing the role of different chemical processes that are relevant in the context of nuclear waste disposal. Applications are for instance to determine the solubility limits for different radioactive elements under different chemical conditions, and to investigate the influences of various mineral phases on the groundwater composition at candidate waste disposal sites. The thermodynamic modelling framework rests on a scientifically well-established basis, which under given circumstances may contribute a great deal to the credibility of long-term predictions in safety assessment work.

Thermodynamic data published in the open scientific literature has during the last few decades been extensively reviewed in different contexts. A number of quality criteria has been proposed during this time. It is in many cases convenient to develop a project specific database, since different requirements are associated with different applications of thermodynamic modelling. It is important that quality requirements are considered as thoroughly during the final step of gathering data from different sources as during the previous steps (experimental work, treatment of experimental data, review and compilation of literature data etc.). The concept of internal consistency is addressed in detail in this report, which is one of several reliability requirements that should be used to assess the quality of a database. It is important to point out, however, that the requirements of internal consistency must be related to other reliability requirements such as accuracy and completeness.

Relevance for SKI

The purpose of this report is to be part of the basis for SKI's review of how SKB uses thermodynamic data in site evaluation and safety assessment work.

Results

This report describes the concept of internal consistency and illustrates its importance in a sufficiently clear and comprehensive manner. Two well-known thermodynamic databases are used to exemplify the concept (OECD/NEA and SUPCRT)

Future work

In the area of thermodynamic modelling, additional work is needed to arrive at a more complete description of quality requirements that should be considered in the future reviews of thermodynamic calculations and databases.

Project information

SKI project manager: Bo Strömberg
Project identification number: 01166

Sammanfattning

Denna rapport inriktar sig på konceptet inneboende överensstämmelse i termodynamiska databaser och relevansen av detta koncept för säkerhetsanalyser i samband med slutförvaring av kärnavfall. Förutom att ha egenskapen inneboende överrensstämmelse skall en tillförlitlig databas även vara tillräckligt noggrann över relevanta intervall för tryck och temperatur. En databas skall vara komplett så till vida att alla viktiga förekomstformer i vattenlösning, gaser och fasta faser finns representerade. Dessutom skall data kunna spåras till de ursprungliga experimentella resultaten. Det finns dock ingen unik definition av inneboende överensstämmelse som behöver accepteras rent allmänt som den mest tillämpliga för alla förutsättningar. En konsekvens av detta är att två databaser som var för sig innehar egenskapen inneboende överensstämmelse kan vara inkonsekventa i förhållande till varandra, och att en databas som är härledd från två eller flera databaser måste i egen egenskap uppfylla konceptet inneboende överensstämmelse.

Konsekvenserna av att använda alternativa definitioner som rimligtvis kan anses bero på konceptet inneboende överensstämmelse kan illustreras med hjälp av databasen som understödjer SKB:s nyligen publicerade säkerhetsrapport SR97. Denna databas uppfyller ej kravet inneboende överrensstämmelse eftersom den innehåller jämviktskonstanter som beräknats över ett intervall av temperaturer:

- användning av motstridiga referensvärden för vissa fasta faser, gaser och lösta ämnen som är vanliga i två databaser med inneboende överensstämmelse (OECD/NEA databasen för radioelement och SUPCRT databasen för icke-radioaktiva element) som används som källor för databasen i SR97,

- användning av olika definitioner i dessa källdatabaser av standard tillstånd för kondenserade faser och lösta species,

- olika matematiska uttryck används i dessa två källdatabaser för att representera temperaturberoendet av värmekapaciteten, och

- olika kemiska modeller används i dessa källdatabaser för vattenfasen.

Betydelsen av dessa typer av inkonsekvenser måste dock relateras till andra tillförlitlighetskrav som omnämns ovan. Att acceptera en viss avvikelse från konceptet inneboende överensstämmelse är sålunda troligtvis att föredra framför att använda en databas som karakteriseras av inneboende överensstämmelse men som inte är tillräckligt noggrann eller är inkomplett. I dessa fall måste i varje fall avvikelserna från konceptet inneboende överensstämmelse dokumenteras och minimeras så långt som möjligt för att erhålla förtroende för beräknade resultat.

Summary

This report addresses the concept of internal consistency and its relevance to the reliability of thermodynamic databases used in repository safety assessments. In addition to being internally consistent, a reliable database should be accurate over a range of relevant temperatures and pressures, complete in the sense that all important aqueous species, gases and solid phases are represented, and traceable to original experimental results. No single definition of internal consistency need be universally accepted as the most appropriate under all conditions, however. As a result, two databases that are each internally consistent may be inconsistent with respect to each other, and a database derived from two or more such databases must itself be internally inconsistent.

The consequences of alternative definitions that are reasonably attributable to the concept of internal consistency can be illustrated with reference to the thermodynamic database supporting SKB's recent SR 97 safety assessment. This database in internally inconsistent because it includes equilibrium constants calculated over a range of temperatures:

- using conflicting reference values for some solids, gases and aqueous species that are common to two internally consistent databases (the OECD/NEA database for radioelements and SUPCRT databases for non-radioactive elements) that serve as source databases for the SR 97 TDB,

- using different definitions in these source databases of standard states for condensed phases and aqueous species,

- based on different mathematical expressions used in these source databases representing the temperature dependence of the heat capacity, and

- based on different chemical models adopted in these source databases for the aqueous phase.

The importance of such inconsistencies must be considered in relation to the other database reliability criteria noted above, however. Thus, accepting a certain level of internal inconsistency in a database is probably preferable to using a database that is internally consistent but inaccurate or incomplete. In such cases, the inconsistencies should at least be documented and minimized to the extent possible to enhance confidence in calculated results.

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1　Introduction

The objective in preparing this report was originally to identify issues that could affect the reliability of thermodynamic databases supporting safety assessments of the KBS-3 disposal concept for spent nuclear fuel. The data in a reliable thermodynamic database should be internally consistent, accurate over a range of relevant temperatures and pressures, complete in the sense that all important aqueous species, gases and solid phases are represented, and traceable to original experimental results.

It became apparent, however, that confusion regarding the meaning of internal consistency is possible, and that such confusion would limit progress toward any broader discussion of database reliability issues. The scope of the present report is therefore focused on the concept of internal consistency and its consequences for thermodynamic databases used in repository safety assessments.

Slight differences in meaning are in fact reasonably attributable to the concept of internal consistency, and no single definition need be universally accepted as the most appropriate under all conditions. Two databases that are each internally consistent may consequently be inconsistent with respect to each other, and a database derived from two or more such databases must itself be internally inconsistent. It is possible that thermodynamic databases supporting repository safety assessments are internally inconsistent because they are commonly derived from two or more source databases, which may be internally consistent but mutually inconsistent. The basis for this comment is summarized in Section 2, and associated consequences are evaluated in Section 3 with specific reference to the thermodynamic database supporting SKB's recent safety assessment, SR 97 (SKB, 1999). Concluding remarks addressing the importance of internal consistency in relation to the accuracy and completeness of a database are discussed in Section 4.

2   Internal consistency

The International Council for Scientific Unions (ICSU) Committee on Data for Science and Technology (CODATA) provides a clear and internationally accepted description of internal consistency (CODATA, 1982). That description is summarized in Section 2.1. Conclusions that can be drawn from this definition in relation to the internal consistency of thermodynamic databases used in repository safety assessments are discussed in Section 2.2.

2.1   Definitions, importance and practical limitations

Internal consistency is partially defined by criteria that should be met as a database is developed and maintained. These criteria include at least six different requirements (CODATA, 1982; Nordstrom and Munoz, 1985; Nordstrom *et al.,* 1990; Engi, 1992):

- all the data comprising a database are compatible with basic thermodynamic relations and their consequences,

- all the data are derived from one set of reference values (*e.g.,* a reference temperature, T_r, and pressure, P_r, thermodynamic properties of elements and other basic compounds, *etc.*) and constants (*e.g*., gas constant, molecular weights, *etc.*),

- an appropriate choice of standard states is made and applied to all similar substances,

- an appropriate mathematical model is chosen to fit all temperature- and pressure-dependent data,

- an appropriate aqueous chemical model is chosen to fit all aqueous solution data, and

- all relevant experimental data, and types of these data, are represented and considered simultaneously, and conflicts and inconsistencies among experimental measurements are resolved.

These criteria are considered further in Section 3. The main conclusion here is that internal consistency is not *completely* defined until choices are made, and methodologies are selected and adhered to, for each of these criteria (and possibly others). Reasonable differences in these choices and selections are possible depending on the objectives and other practical constraints in developing a database, in which case the internal consistency of two or more databases may be defined slightly differently.

Internal consistency is important because it ensures that there are no sources of ambiguity in the database. Such ambiguities are revealed when mathematical manipulation of the data in various ways results in two (or more) different values for a given thermodynamic

property. The two values are mutually inconsistent, and therefore logically incoherent with respect to the data used to calculate them. If, on the other hand, a database is internally consistent, and all such inconsistencies are therefore resolved, then data that are in conflict with experimental observations can be attributed unequivocally to errors in the data, or to errors in the experimental results. Internal consistency is thus a conditional requirement that must be met before the accuracy of a database can be assessed.

In a more practical sense, internal consistency is perhaps best considered to be an ideal standard that may be closely approached but rarely attained (Engi, 1992). This is because thermodynamic databases are always in need of revision as the results of new experimental studies become available. The close interdependence among the data may require that a substantial portion of a database be revised if even a single new value of an important property is reported. The associated effort required is substantial and mundane, and this tends to discourage progress in sustaining internal consistency as a database is updated and revised. For this reason a tolerable level of inconsistency might be the best that can be hoped for. If so, useful results can still be obtained from thermodynamic calculations because thermodynamic functions such as the equilibrium constant may be accurate in spite of these inconsistencies (Nordstrom *et al.,* 1990; see Section 4.1).

2.2 Internal consistency of thermodynamic databases used in repository safety assessments

The somewhat variable nature of the definition of internal consistency given in Section 2.1 is a potential source of confusion, which could complicate efforts to evaluate the reliability of thermodynamic databases supporting repository safety assessments. These databases are developed in part from several internally consistent "source" databases, but the choices made and methodologies selected to define internal consistency may differ from one source to another. For example, the aqueous chemical model chosen for geochemical databases usually incorporates a solute activity expression appropriate for relatively dilute solutions (*i.e.*, based on ion-association theory) and an equation-of-state for the solvent that is appropriate over a range of pressures and temperatures encountered in the Earth's crust. The model chosen for radiochemical databases, on the other hand, may include an activity model appropriate for highly concentrated solutions (*i.e.,* based on specific ion-interaction theory) and an equation-of-state for H_2O that is limited to relatively low temperatures and pressures compatible with the available experimental database. These two databases might each be internally consistent, but are mutually inconsistent due to the reasonable differences in deciding which aqueous chemical model is most appropriate for the purpose at hand.

Internally consistent databases that are relevant to repository investigations and compatible with the definitions given in Section 2.1 have been developed for radioelements (Grenthe *et al.,* 1992; Silva *et al.,* 1995; Rard *et al.,* 1999; Lemire, 2001), and non-radioactive elements (Helgeson *et al.,* 1978; Robie *et al.,* 1978; Hemingway *et al.,* 1982; Robinson *et al.,* 1983; Halbach and Chatterjee, 1984; Holland and Powell, 1985; Berman *et al.,* 1986; Berman, 1988; Holland and Powell, 1990; Johnson *et al.,* 1992; Saxena *et al.,* 1993; Oelkers *et al.,* 1995; Berman and Aranovich, 1996; Gottschalk, 1997). These databases contain for each mineral, aqueous species or gas a sufficient set of standard-state properties to enable

calculation of any of the respective thermodynamic functions (*e.g.,* log *K*) over as broad a range of pressures and temperatures as possible.

Several of the internally consistent databases noted above serve as primary data sources in thermodynamic databases used in repository safety assessments [*e.g.,* Daveler and Wolery, 1992; Pearson and Waber, 1999; Yui *et al.,* 1999; Spahiu, *per. comm.* (see Section 3)]. The repository databases generally include equilibrium constants for reactions over a range of temperatures. They support most types of geochemical modeling software (*e.g.,* Truesdell and Jones, 1974; Westall *et al.,* 1976; Parkhurst *et al.,* 1980; Wolery, 1992; Allison *et al.,* 1992; Appelo and Postma, 1993), and have been used to conduct safety assessments and RD&D investigations of disposal concepts for spent nuclear fuel and other nuclear wastes (*e.g.,* SKI, 1996; SKB 1999; Vieno and Nordman, 1999; JNC, 2000; DOE, 2001).

The internal consistency of databases used in repository safety assessments is questionable, however, because these databases are derived in part from other internally consistent databases, and because slight differences in the exact definition of internal consistency may be adopted in the source databases. If so, the repository databases must be internally inconsistent in the literal and practical senses discussed in Section 2.1. This possibility is evaluated in the next section.

3 Internal consistency of the SR 97 TDB

The SR 97 thermodynamic database (TDB)[1] supports the EQ3/6 software package (Wolery, 1992). It includes equilibrium constants for mineral hydrolysis, gas-solubility, ion association/dissociation and oxidation-reduction reactions at temperatures up to 300°C at pressures between 1 bar ($T = 0$ to 100°C) and the equilibrium vapor pressure of water ($T > 100$°C). The data come from a variety of sources. Data for many non-radioactive elements, are taken from the ".sup" database, which is included with the EQ3/6 software package and which is derived from calculations using the SUPCRT model and databases (see below). Other primary sources of data for both radioelements and non-radioactive elements are from the Nagra NTB 91-17 and NTB 91-18 databases (Pearson and Berner, 1991 and Pearson *et al.*, 1992, respectively). Additional data for uranium from Puigdomenech and Bruno (1988), for plutonium from Puigdomenech and Bruno (1991), for technetium from Puigdomenech and Bruno (1995), and for lanthanides from Spahiu and Bruno (1995) are included in SR 97 TDB. Bruno *et al.* (1997) also include new or revised thermodynamic data for Ni, Se, Sr, Zr, Ni, Tc, Pd, Ag, Sn, Sm, Ho, Ra, Th, Pa, U, Np, Pu, Am and Cm. Data for many of the aqueous species and/or solid phases of Br, I, Cl, N, Si, Tc, Am, Np and U are taken from the Organisation for Economic Cooperation and Development (OECD) Nuclear Energy Agency (NEA) Thermochemical Data Base (TDB) project (Östhols and Wanner, 2000).

3.1 Approach

The SR 97 TDB includes data from at least two internally consistent databases: the SUPCRT databases and databases[2] developed by the OECD/NEA. Sources of internal *in*consistency in the SR 97 database are thus directly attributable to different choices and methodologies used to define the criteria that establish thermodynamic consistency in these two source databases (Section 2.1). The following discussion therefore addresses whether there are any differences in these choices for each of the defining criteria adopted in the OECD/NEA and SUPCRT databases. The SUPCRT model and databases are described in Appendix 1. The database developed by the OECD/NEA TDB project is described in Appendix 2.

3.2 Thermodynamic relations and their consequences

All thermodynamic functions are related through equations derived from the basic laws of thermodynamics and the ideal gas law. The OECD/NEA TDB project uses this fact in a database system and associated software to consistently derive thermodynamic data at standard conditions, and to internally recalculate the data when a change is made to the value of one or more parameters (*e.g.,* Silva *et al.*, 1995). The internal recalculations are

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[1] A copy of this database was kindly provided to the author by K. Spahiu (SKB).
[2] The criteria adopted for thermodynamic consistency in all these databases are equivalent, and they are therefore considered as a single database for discussion purposes in the present report.

presumably also constrained by the requirement that all revised parameter values must remain consistent with the available experimental dataset.

The requirement of simultaneous consistency with respect to both thermodynamic relations and all relevant experimental data is satisfied for minerals in the SUPCRT databases using matrix analytical methods to set up a general optimization problem involving simultaneous evaluation of experimental data for multiple reactions. This approach ensures that all thermodynamic parameters are internally consistent and also consistent with the experimental data upon which they are based.

An example illustrating the use of the matrix approach is of general interest because it reveals two problems that may complicate efforts to establish and maintain internal consistency in a database. Powell and Holland (1985) adopt a regression method based on experimentally determined enthalpies of reaction involving a number of different minerals to construct the following constraint matrix:

$$\mathbf{b} = \mathbf{Rh}, \tag{1}$$

where $\mathbf{R}$ denotes the matrix of stoichiometric coefficients among the set of reactions, $\mathbf{h}$ stands for the vector of enthalpies of formation for each of the minerals considered (*i.e.*, these are the primary values being calculated in this example), and $\mathbf{b}$ refers to the vector of experimentally based reaction enthalpies.

The objective of the calculations is to minimize values of the following quantity:

$$\left\| \mathbf{b} - \mathbf{Rh} \right\|^2 \tag{2}$$

which, in this example involving high albite (*ab*), paragonite (*pa*), andalusite (*and*), kyanite, (*ky*), jadeite (*jd*), corundum (*cor*), quartz (*q*) and water (H_2O) is given by:

$\mathbf{h}^T =$ enthalpies of formation of

[*ab* *pa* *and* *ky* *jd* *cor* *q* H_2O]

$\mathbf{R} =$
|1 0 0 0 -1 0 -1 0 |
|0 -1 0 1 1 0 0 1 |
|1 -1 0 0 0 1 0 1 |
|1 -1 1 0 0 0 -1 1 |
|1 -1 0 1 0 0 -1 1 |

$\mathbf{b} =$
|$\Delta H^\circ_{r,P,T}$ (*jd+q = ab*) |
|$\Delta H^\circ_{r,P,T}$ (*pa = jd+ky+H₂O*) |
|$\Delta H^\circ_{r,P,T}$ (*pa = ab+cor+H₂O*) |
|$\Delta H^\circ_{r,P,T}$ (*pa+q=ab+and+H₂O*) |
|$\Delta H^\circ_{r,P,T}$ (*pa+q = ab+ky+H₂O*) |

This problem cannot be solved, however, because there are five equations (fixing the enthalpies of reaction) and eight unknowns (enthalpies of formation of *ab, pa, and, ky, jd,*

cor, q, and *H₂O*). To overcome this problem, Powell and Holland (1985) expand **R** by six rows of the form:

[0,0,...0,1,0,..,0,0]

where the value, 1, is centered on the position of an "anchor" mineral, for which a corresponding row in **b** is added containing a calorimetrically determined reference value for the enthalpy of formation of the anchor phase. The anchor minerals in this example are assumed to be *and, ky, jd, cor, q* and *H₂O*, for which calorimetric values for the enthalpy of formation at 1 bar and 25°C from Robie *et al.* (1978) are used to calculate enthalpies of formation for *ab* and *pa*. This approach ensures that the calculated enthalpies of formation for *ab* and *pa* are internally consistent with respect to the enthalpies of formation of *and, ky, jd, cor, q* and *H₂O*, and are also consistent with all the experimentally determined enthalpies of reaction contained in the reaction vector, **b**.

A potential problem associated with the matrix approach is illustrated by this example, *i.e.,* an error in any one datum must be propagated throughout the database. The data for minerals in the SUPCRT databases (*i.e.,* from Helgeson *et al.*, 1978) may suffer from this problem (Nordstrom and Munoz, 1985). Standard molal Gibbs free energies and enthalpies of formation for aluminous minerals in this database contain a systematic error of 1.55 kcal mol^{-1}, which was traced by Hemingway *et al.* (1982) to the use of an incorrect value adopted for the enthalpy of reaction for kaolinite + H_2O = 2 gibbsite + 2 $SiO_2(aq)$. The incorrect value is used by Helgeson *et al.* (1978) to calculate the enthalpy of formation of kaolinite. Kaolinite is adopted as a reference mineral in this database, and the error is therefore propagated through all aluminous phases.

A second problem with the approach is that it is cumbersome and may therefore be difficult to apply as the system considered becomes more and more complex. The above example considers a relatively simple system of seven minerals and a simple fluid phase consisting only of H_2O. In contrast, systems considered in safety assessments are multicomponent, multiphase systems, and the fluid phase is itself a complex aqueous solution.

In summary, both the OECD/NEA and SUPCRT databases are consistent with basic thermodynamic relations and their consequences. Mathematical manipulation of these relations in various ways should therefore not result in two or more different values for a given thermodynamic property. Although such "consistency checks" are relatively easily implemented in computerized database programs, they do not necessarily ensure that all the data also remain consistent with the available experimental database. Matrix analytical methods can be used to ensure that a database is simultaneously consistent with basic thermodynamic relations and the experimental database, but implementation of such methods may be extremely difficult to carry out in practice.

3.3   Reference values and constants

The OECD/NEA and SUPCRT databases include a number of minerals, gases and aqueous species that are common to both databases. These primary, or "core", thermodynamic data in the OECD/NEA TDB contain primarily CODATA key values (Cox *et al.*, 1989), and

additional data for uranium compounds recommended by Grenthe *et al.* (1992). Corresponding data in the SUPCRT databases also include CODATA key values and data from other sources (Appendix 1). The core data are used to calculate equilibrium constants in the SR 97 TDB. Equilibrium constants derived from the OECD/NEA database would not be consistent with equilibrium constants derived from the SUPCRT databases if the core data common to both databases are not identical within stated uncertainty limits.

Uncertainties in the OECD/NEA databases are assigned to the core data at the statistically defined 95% confidence interval (Wanner and Östhols, 1999). Absolute uncertainties in the SUPCRT databases have not been estimated, however. This is because attempts to assign uncertainties to these data are considered to be unrealistic due to the multiple sources of uncertainty and ambiguity in interpretive methods used to retrieve the data from experimental results, and to additional limitations imposed by the matrix analytical methods used to evaluate the thermodynamic properties of multiple reactions simultaneously (Helgeson *et al.*, 1978). For these reasons it is considered preferable not to assign absolute uncertainties to the SUPCRT data, rather than to estimate uncertainties that may be both inaccurate and misleading.

To compare core values in the OECD/NEA and SUPCRT databases it must therefore be conservatively assumed that these databases are consistent with one another if reported values in the SUPCRT database lie within the range of uncertainties assigned to corresponding values in the OECD/NEA database. Arthur *et al.* (1999) have carried out such comparisons, and results are summarized in the following paragraphs.

Solid phases that are common to the OECD/NEA and SUPCRT databases include $Cu(c)$, $C(c)$ (graphite), corundum, lime, periclase and α-quartz. The standard molal entropy of lime in the SUPCRT databases (9.5 cal mol^{-1} K^{-1}) differs from the corresponding nominal value and associated uncertainty limits in the OECD/NEA database (9.106 ± 0.096 cal mol^{-1} K^{-1}). The data for solid phases are otherwise consistent with respect to the OECD/NEA assigned uncertainty limits.

Discrepancies between the OECD/NEA and SUPCRT databases in standard molal and partial molal Gibbs free energies and enthalpies of formation (ΔG^o_f and ΔH^o_f, respectively) and standard entropies (S^o) for aqueous species and gases are shown in Figs. 1 – 3, respectively. The ordinate in these figures refers to the respective value in the SUPCRT databases minus the corresponding nominal value in the OECD/NEA database. When this difference exceeds uncertainty limits assigned to the nominal value in the latter database (indicated by the error bars in the figures), this is taken to mean that the respective data in the SUPCRT and OECD/NEA databases are discrepant.

As can be seen in Fig. 1, discrepancies in ΔG^o_f are apparent for:

- Al^{3+}, Ba^{2+}, Br^-, HF_2^-, $H_3PO_4(aq)$, $H_2PO_4^-$, HPO_4^{2-}, $HSeO_3^-$, I^-, IO_3^-, Mg^{2+}, OH^-, PO_4^{3-}, $S_2(g)$, and SO_4^{2-}.

Discrepancies in ΔH^o_f, as shown in Fig. 2, are evident for:

8
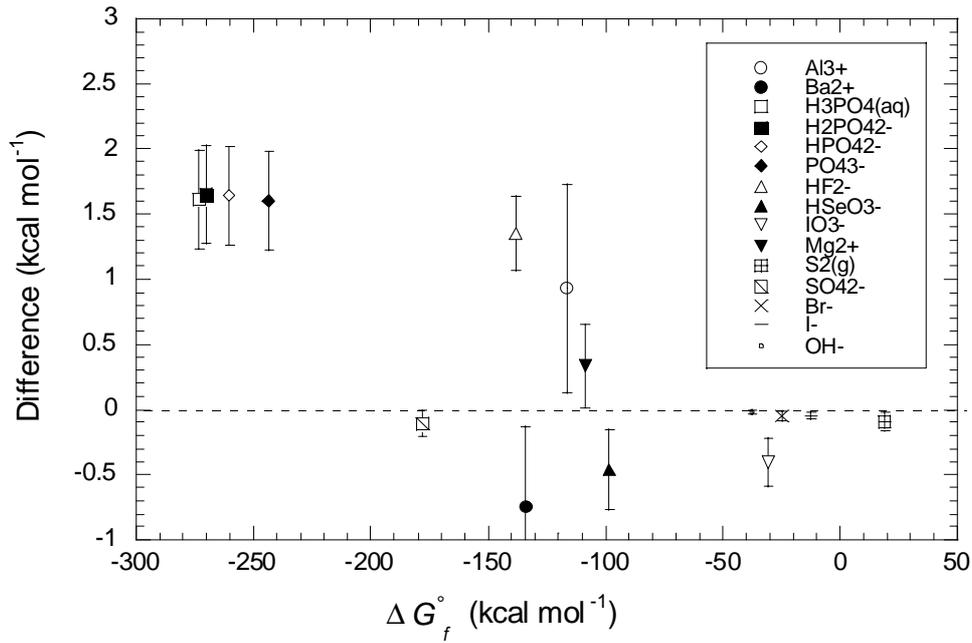
Figure 1. Differences in standard Gibbs free energies of formation of aqueous species and S₂(g) in the SUPCRT and OECD/NEA thermodynamic databases at 25°C and 1 bar versus ΔG°f for each species or gas in the SUPCRT TDB (from Arthur et al., 1999).
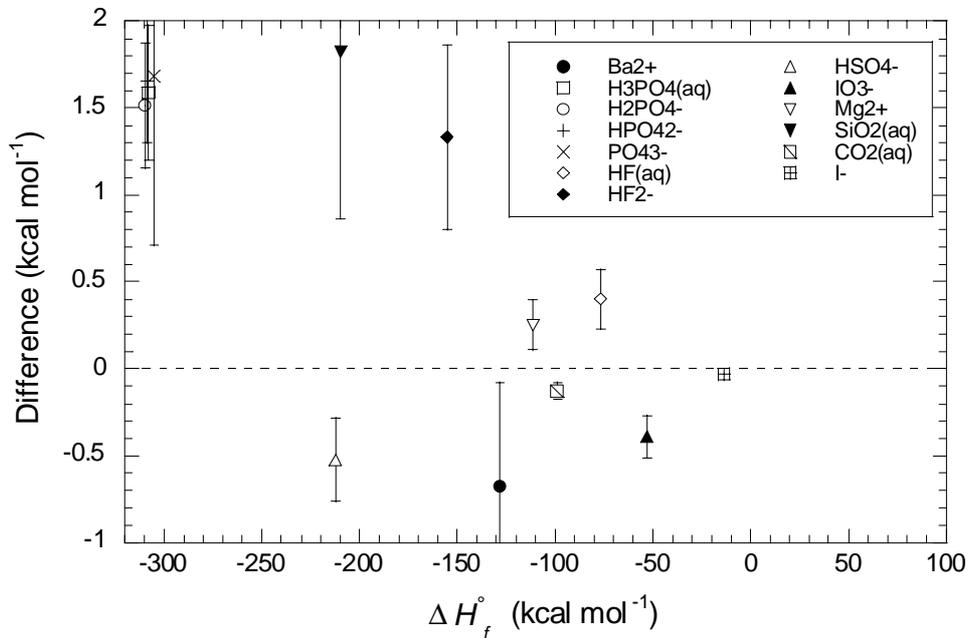
Figure 2. Differences in standard partial molal enthalpies of formation of aqueous species in the SUPCRT and OECD/NEA thermodynamic databases at 25°C and 1 bar versus ΔH°f for each species in the SUPCRT TDB (from Arthur et al., 1999).
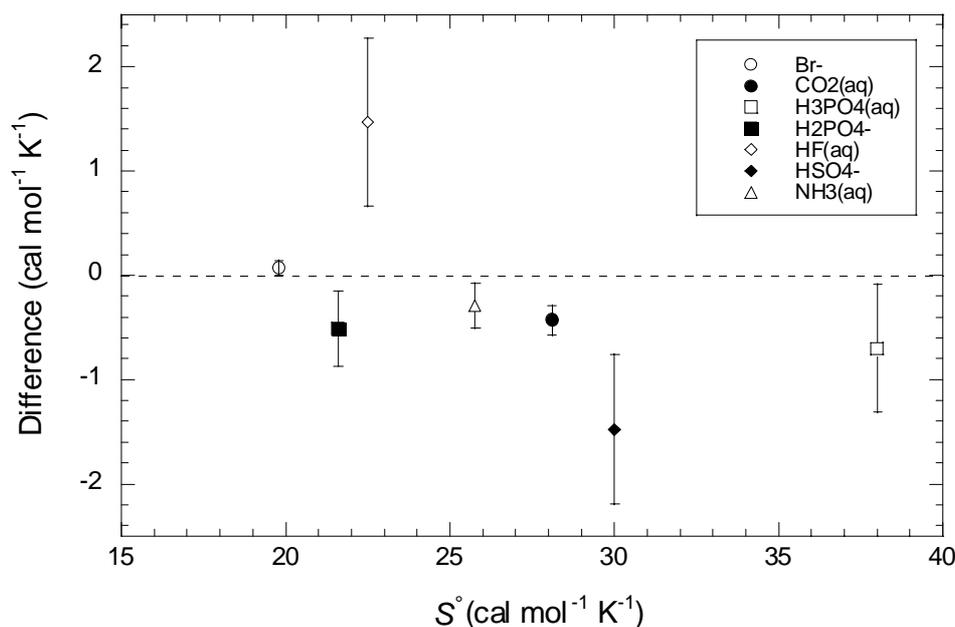
Figure 3. Differences in standard partial molal entropies of aqueous species in the SUPCRT and OECD/NEA thermodynamic databases at 25°C and 1 bar versus S° for each species in the SUPCRT TDB (from Arthur et al., 1999).

- Ba^{2+}, $CO_2(aq)$, $HF(aq)$, HF_2^-, $H_3PO_4(aq)$, $H_2PO_4^-$, HPO_4^{2-}, HSO_4^-, I^-, IO_3^-, Mg^{2+}, PO_4^{3-} and $SiO_2(aq)$.

Standard entropies (Fig. 3) are discrepant for the following species:

- Br^-, $CO_2(aq)$, $HF(aq)$, $H_3PO_4(aq)$, $H_2PO_4^-$, HSO_4^- and $NH_3(aq)$.

The core data in the OECD/NEA and SUPCRT databases are thus conservatively discrepant for one solid, one gas and for several aqueous species. Equilibrium constants in the SR 97 TDB calculated for reactions involving this solid or gas, and these aqueous species, using the OECD/NEA and SUPCRT databases must therefore be inconsistent.

The significance of these discrepancies is difficult to assess, however. It is likely that estimates of absolute uncertainties in the SUPCRT databases, although possibly ill-advised for reasons noted above, would eliminate most of the discrepancies noted above, but probably not all [*e.g.*, for the phosphate species and for $SiO_2(aq)$]. Thus resolving inconsistencies in the SR 97 TDB arising from these differences in reference values may require re-evaluating whether accurate and unambiguous absolute uncertainties in the SUPCRT databases can be realistically assigned.

3.4 Standard states

The standard state chosen for gases in both the OECD/NEA and SUPCRT databases is identical, but the standard states chosen for condensed phases (pure solids and liquids) and

aqueous species are not (see Appendixes 1 and 2). The standard state for gases is unit fugacity for the pure gas or gas mixture in a (hypothetical) state in which it exhibits ideal gas behavior at 1 bar (0.1 MPa) and any temperature.

For a pure solid, the OECD/NEA database adopts a standard state of unit activity for the pure solid at any temperature and the standard-state pressure (1 bar). The SUPCRT database chooses unit activity for thermodynamic components that are stoichiometrically equivalent to the pure solid at any temperature and pressure.

For a pure liquid, the OECD/NEA database adopts a standard state of unit activity of the (ordinarily) pure liquid at any temperature and the standard-state pressure. The SUPCRT database calls for a standard state of unit activity for the pure liquid at any temperature and pressure.

For a solute in solution, the OECD/NEA database chooses unit activity of the solute in a hypothetical ideal 1 molal solution referenced to infinite dilution at any temperature and the standard-state pressure. The SUPCRT database adopts unit activity in a hypothetical ideal 1 molal solution referenced to infinite dilution at any temperature and pressure.

The standard states adopted for condensed phases and solutes in the OECD/NEA and SUPCRT databases thus differ because a fixed-pressure standard state is chosen in the former, whereas a variable-pressure standard state is adopted in the latter. Equilibrium constants calculated using the OECD/NEA database are thus pressure independent, whereas equilibrium constants calculated using the SUPCRT database are pressure dependent. The corresponding difference in the value of an equilibrium constant calculated for a given reaction (assuming equivalent data for the relevant reactants and products in both databases) is given by (*e.g.* Anderson and Crerar, 1993):

$$\ln K_{P_2} - \ln K_{P_1} = -\frac{\Delta_s V^{\circ}}{RT}(P_2 - P_1) - \frac{1}{RT}\int_{P_1}^{P_2} \Delta_r V^{\circ}(aq)dP, \tag{3}$$

where K stands for the equilibrium constant at pressure P_2 ($\neq$ 1 bar) and P_1 (= 1 bar), $\Delta_s V^{\circ}$ represents the change in volume among product and reactant solid phases, $\Delta_r V^{\circ}(aq)$ denotes the change in partial molar volume among product and reactant aqueous species, R stands for the gas constant and T represents temperature[3].

It is assumed in the SR 97 TDB that the total pressure equals 1 bar at $T \leq 100°C$, in which case equilibrium constants calculated using the OECD/NEA and SUPCRT databases must be identical (again, assuming equivalent data for reactants and products in both databases). Equilibrium constants would not be equivalent at temperatures greater than 100°C, however, because the total pressure is then assumed to be equal to the equilibrium vapor pressure of water. Actual differences in the calculated equilibrium constants under these conditions are probably small, and possibly negligible, because the equilibrium vapor pressure of water does not increase significantly at temperatures up to 300°C (*i.e.,* the upper

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[3] No general expression exists for the volume integral in this equation. The effect of pressure on partial molar volume is expressed in the form of an analytical expression derived either empirically or from a model, such as the revised HKF model used in SUPCRT (Appendix 1).

temperature limit in the SR 97 TDB), and because the volume and partial molar volume changes among solid phases and aqueous species are generally small.

3.5 Mathematical models of pressure- and temperature-dependent data

The temperature dependence of the standard molar heat capacity at constant pressure $[C_{p,m}(T)]$ for a pure solid, gas or aqueous species, m, is represented in the OECD/NEA database by an empirical function given by (*e.g.,* Östhols and Wanner, 2000):

$$C^{\circ}_{p,m}(T) = a + bT + cT^2 + jT^3 + dT^{-1} + eT^{-2} + kT^{-3} + f \ln T + gT \ln T$$
$$+ h\sqrt{T} + i\frac{1}{\sqrt{T}}, \tag{4}$$

where the symbols *a, b, c, etc.*, denote empirical coefficients[4]. This temperature function can be used with the corresponding standard molar entropy, and the standard molar Gibbs free energy and enthalpy of formation at the reference temperature (25°C) and standard-state pressure (1 bar), to calculate thermodynamic properties and functions at temperatures other than 25°C (see Puigdomènech *et al.,* 1997).

Conventional standard partial molal heat capacities of aqueous ions in the SUPCRT databases are considered in terms of solvation and non-solvation contributions described by the following semi-empirical equation (*e.g.,* Tanger and Helgeson, 1988):

$$\overline{C}^{\circ}_P(P,T) = c_1 + \frac{c_2}{(T-\Theta)^2} - \left[\frac{2T}{(T-\Theta)^3}\right]\left[a_3(P-P_r) + a_4 \ln\left(\frac{\Psi+P}{\Psi+P_r}\right)\right]$$
$$+ \omega TX + 2TY\left(\frac{\partial\omega}{\partial T}\right)_P - T\left(\frac{1}{\varepsilon}-1\right)\left(\frac{\partial^2\omega}{\partial T^2}\right)_P. \tag{5}$$

In this equation c_1, c_2 and $a_1 - a_4$ refer to empirical pressure - and temperature (T)-independent non-solvation coefficients that are specific to each aqueous ion, Ψ and Θ denote pressure- and temperature-independent constants equal to 2600 bar and 228°K, respectively, P and P_r represent the pressure and reference pressure, respectively, ω stands for the solute's conventional born coefficient, X and Y denote born functions for the solvent and ε refers to the solvent's dielectric constant. For minerals and gases, the SUPCRT databases use the empirical Maier-Kelley function (Maier and Kelley, 1932) to represent the temperature dependence of the standard molal heat capacity:

$$C^{\circ}_P = a + bT + cT^{-2}, \tag{6}$$

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[4] The coefficients *a, b, c* (or *d*) and *e* are most often used, *i.e.,* the other coefficients are then assigned a value = 0 (Östhols and Wanner, 2000).

where *a*, *b*, and *c* refer to empirical temperature-independent coefficients[5]. The temperature and pressure function given by Eqn. (5) and the temperature function given by Eqn. (6) can be used with the relevant standard molal and partial molal entropies, and standard molal and partial molal Gibbs free energies and enthalpies of formation at the reference temperature (25°C) and reference pressure (1 bar), to calculate thermodynamic properties and functions at temperatures and pressures other than 25°C and 1 bar (*e.g., Johnson et al., 1992*).

The mathematical models used in OECD/NEA and SUPCRT databases to represent the pressure- and temperature-dependence of thermodynamic properties and functions differ significantly, as can be seen by comparing Eqn. (4) with Eqns. (5) and (6). For aqueous ions, the empirical temperature function given by Eqn. (5) differs significantly from the semi-empirical temperature- and pressure-dependent function given by Eqn. (4). For minerals and gases, the temperature-dependent functions would only be identical in form if the coefficients *a, b* and *e* in Eqn (4) and coefficients *a b* and *c* in Eqn. (5) are used.

3.6   Aqueous solution models

The aqueous solution models adopted in the OECD/NEA and SUPCRT databases differ fundamentally in several respects. Significant differences in the approach used to account for the pressure- and temperature-dependence of thermodynamic properties are alluded to in the preceding section, and are discussed in more depth in the references noted in Appendixes 1 and 2.

The solution models adopted to develop these databases also differ fundamentally in terms of the approach used to describe the ionic medium dependence of equilibrium constants. The approach used to develop the OECD/NEA database takes into account individual characteristics of the ionic media using a medium dependent expression for the activity coefficients of aqueous species involved in the equilibrium reaction. This expression comes from specific ion interaction theory in the form of the Bronsted-Guggenheim-Scatchard approach (*e.g., Grenthe et al., 1997*). The medium dependence is described by virial or ion-interaction coefficients. No data characterizing individual ionic processes are required, or derived, in this approach. These processes are expressed by the magnitudes of the ion-interaction coefficients.

The approach used to develop the SUPCRT databases adopts an extended Debye-Hückel expression, in which the activity coefficients of the reactants and products depend only on the ionic charge and ionic strength (*Helgeson et al., 1981*). Medium-specific interactions are accounted for by introducing ionic pairing between the ions of the medium and the species involved in the equilibrium reactions. This approach is thus more reaction-oriented than that used to develop the OECD/NEA databases, and it enables the thermodynamic properties of individual ions to be calculated over a much broader range of temperatures and pressures. The approach relies on empirical coefficients, but the coefficients are interrelated by standard thermodynamic equations.

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[5] This equation is only valid for minerals that do not experience a phase transition over the range of temperatures considered. Similar equations are used for minerals that do experience phase transitions, together with the enthalpy and volume change at the transition temperature.

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Both approaches discussed above use empirical coefficients and other constants (*e.g.*, ion-pairing constants in SUPCRT approach) to retrieve values of equilibrium constants and other thermodynamic properties at the reference state of infinite dilution. The retrieved data are thus somewhat model dependent because they depend on the values selected for these coefficients and constants. The OECD/NEA and SUPCRT databases are thus each internally consistent but may also be mutually inconsistent insofar as the choices made in selecting these coefficients and constants differ.

3.7 Data representation and resolution of conflicts and inconsistencies

The OECD/NEA and SUPCRT databases are developed using the same basic procedures to retrieve values of thermodynamic properties from experimental data. These procedures are documented by the OECD/NEA TDB project (Wanner and Östhols, 1999; Wanner and Östhols, 2000), and in numerous publications describing the SUPCRT model and its databases (Appendix 1). The procedures are based on mathematical/statistical techniques used to identify experimental data that are discordant with respect to other data, or other data sets, combined with expert judgment to evaluate whether the discordant values are due to inadequate experimental technique or inadequate documentation. If so, the discordant values are eliminated. If not, uncertainties may be relaxed such that the discordant data are accorded less weight in regression techniques used to retrieve values of thermodynamic parameters.

Data from all available types of experimental data are represented to the extent possible in the SUPCRT databases because it has become increasingly evident that subsets of preferred experimental technique are never sufficiently precise to define fully all thermodynamic properties (Berman, 1988). This view is based in part on the work of Helgeson *et al.* (1978), who realized that enthalpies of formation had not generally been determined calorimetrically with the accuracy needed to reproduce the results of high-temperature and high-pressure phase-equilibrium experiments. Internally consistent databases for non-radioactive elements developed since 1978 are therefore constrained by both phase-equilibrium data and a limited amount of reference calorimetric values. More recently it has been shown that thermodynamic properties retrieved from solubility and mineral-stability experiments at relatively low-temperatures and pressures are in some cases inconsistent with data retrieved from both calorimetric and phase-equilibrium studies (Sverjensky *et al.*, 1991; Pokrovskii and Helgeson, 1995; 1997b). This suggests that reliable thermodynamic data must be constrained by all available types of experimental data spanning as broad a range of temperatures and pressures as possible.

In contrast, experimental data represented in the OECD/NEA databases are generally limited to low temperatures (*i.e.,* about 25ºC) due to experimental difficulties that are inherent in working with radioactive materials at higher temperatures and pressures. It is therefore not possible to assess whether retrieved values of thermodynamic properties for radioactive elements are similarly consistent over the broad range of temperatures and pressures considered in databases for non-radioactive elements.

4 Concluding remarks

Thermodynamic databases supporting repository safety assessments may not be internally consistent because they commonly include equilibrium constants calculated using two or more source databases that may be internally consistent but mutually inconsistent. The SR 97 TDB is not internally consistent, for example, because it includes equilibrium constants calculated using the OECD/NEA and SUPCRT source databases, and because reasonable differences in definitions of internal consistency are adopted in these source databases. The SR 97 TDB thus includes equilibrium constants that are calculated:

- using values for common parameters in the two source databases that disagree in some cases relative to uncertainty limits assigned to nominal values in the OECD/NEA database,

- using different definitions of standard states for condensed phases and aqueous species,

- based on different mathematical expressions representing the temperature dependence of the heat capacity, and

- based on different chemical models for the aqueous phase.

Such inconsistencies may undermine confidence in the results of safety assessments, and should therefore be acknowledged and minimized to the extent possible. This could be a formidable task, however, because a common definition of internal consistency would have to be implemented in every source database used, which would entail recalculation of all affected parameter values to ensure that they remain consistent with thermodynamic relations and their consequences, and with the experimental data upon which they are based.

Although thermodynamic databases used in repository safety assessments may be internally inconsistent, it is important to emphasize that the importance of such inconsistencies must be considered in relation to other database reliability issues. Thus, accepting a certain level of internal inconsistency in a database may be preferable to using a database that is internally consistent but inaccurate or incomplete. Comments addressing the relative importance of internal consistency versus database accuracy and database completeness are summarized below.

4.1 Consistency versus accuracy

The accuracy of calculated thermodynamic functions does not depend on the internal consistency of the database upon which the calculations are based. Internal consistency is only a conditional requirement that must be met before the accuracy of a database can be assessed. Equilibrium constants calculated using two internally consistent, but mutually inconsistent, databases may therefore closely agree with each other and with the available

experimental evidence. Thus, although a database may be internally inconsistent, this does not mean it is inaccurate.

The relation between the accuracy and internal consistency of thermodynamic databases is evaluated by Arthur *et al.* (1999), who compare standard molal volumes and entropies, and standard molal Gibbs free energies and enthalpies of formation, at 25°C and 1 bar for minerals of non-radioactive elements that are common to internally consistent databases developed by Helgeson *et al.* (1978), Berman (1988), Holland and Powell (1990), Johnson *et al.* (1992) and Oelkers *et al.* (1995). The accuracy of all these databases is extensively verified in well-documented comparisons of calculated thermodynamic functions (*e.g.*, equilibrium constants, phase-equilibrium reversal temperatures) with their experimental counterparts (*e.g.,* experimental solution compositions, univariant/divariant equilibrium curves) over a wide range of temperatures and pressures. Comparison of the values of thermodynamic parameters among any two of the databases is therefore of interest because any discrepancies must be related to differences in the respective definitions of internal consistency rather than accuracy.

Results are summarized in Figs. 4 – 7, where, for convenience, the abbreviations 78HEL, 88BER, 90HOL, 91JOH and 95OEL refer to Helgeson *et al.* (1978), Berman (1988) Holland and Powell (1990), Johnson *et al.* (1992), and Oelkers *et al.* (1995), respectively. Mineral names are abbreviated in the figures as follows:

- elements - gph (graphite), iron (elemental Fe),

- oxides - bcri (beta cristobalite), coe (coesite), cor (corundum), hem (hematite), ilm (ilmenite), lime [CaO(c)], mt (magnetite), mang (manganosite), per (periclase), q (quartz), bq (beta quartz), ru (rutile), sp (spinel),

- hydroxides - br (brucite), dia (diaspore),

- carbonates - arag (aragonite), cc (calcite), dol (dolomite), fdol (Fe-dolomite) mag (magnesite), rhc (rhodocrosite), sid (siderite), and

- silicates - acm (acmite), ak (akermanite), ab (albite), abh (albite-high), abl (albite-low), alm (almandine), and (andalusite), andr (andradite), ann (annite), an (anorthite), ant (antigorite), anth (anthophyllite), cap (Ca-Al pyroxene), cel (celadonite), chr (chrysotile), clin (clinochlore), cz (clinozoisite), crd (cordierite), cumm (cummingtonite), di (diopside), ed (edenite), ep (epidote), fa (fayalite), fo (forsterite), fs (ferrosilite), geh (gehlenite), gl (glaucophane), gr (grossular), grun (grunerite), hed (hedenbergite), jd (jadeite), kao (kaolinite), ksp (K-feldspar), kals (kalsilite), ky (kyanite), law (lawsonite), ma (margarite), me (meionite), merw (merwinite), mont (monticellite), mu (muscovite), ne (nepheline), pa (paragonite), parg (pargasite), phl (phlogopite), pre (prehnite), pswo (pseudo-wollastonite), py (pyrope), pyhl (pyrophyllite), san (sanidine), sill (sillimanite), sph (sphene), ta (talc), tr (tremolite) and wo (wollastonite).
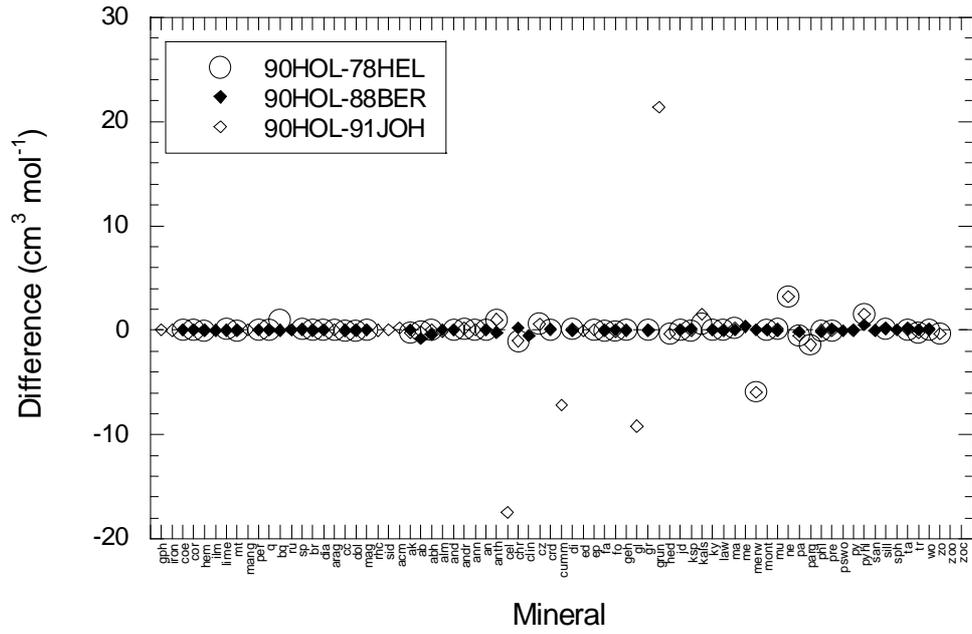
Figure 4. Differences in standard volumes of minerals between the 90HOL and 78HEL, 88BER and 91JOH databases.
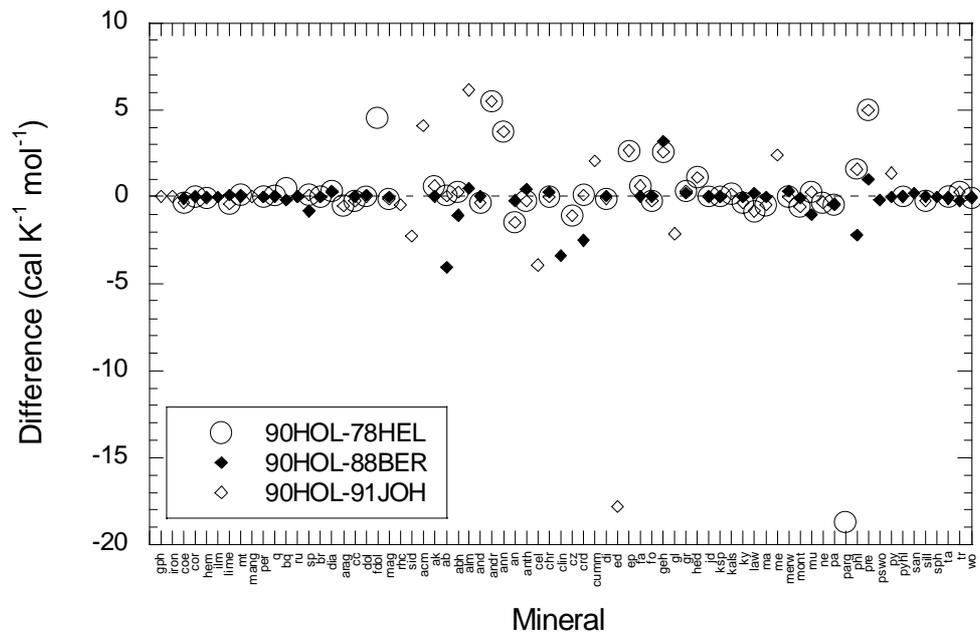
Figure 5. Differences in standard entropies of minerals between the 90HOL and 78HEL, 88BER and 91JOH databases.
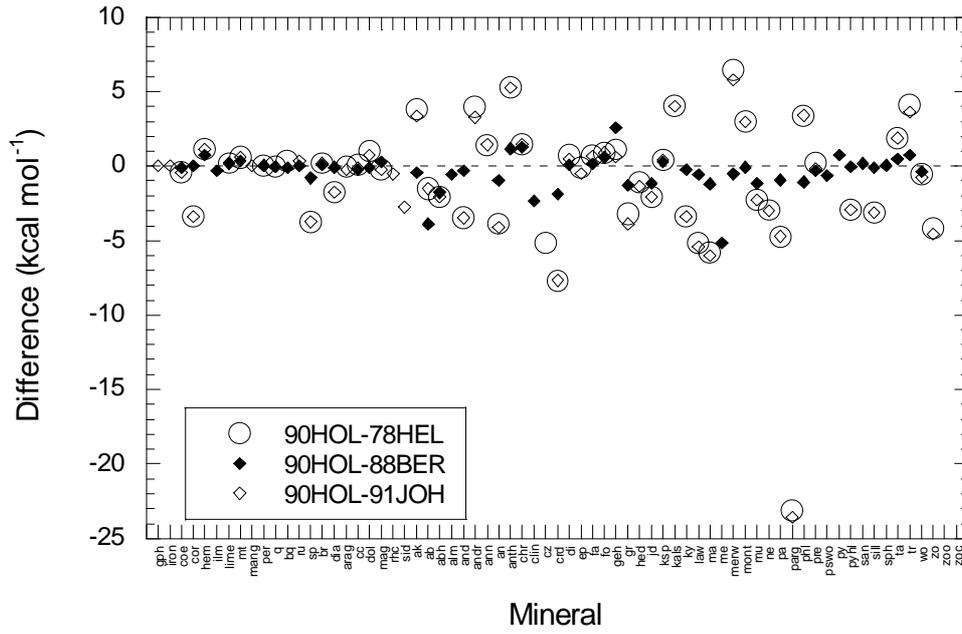
Figure 6. Differences in standard enthalpies of formation of minerals between the 90HOL and 78HEL, 88BER and 91JOH databases.
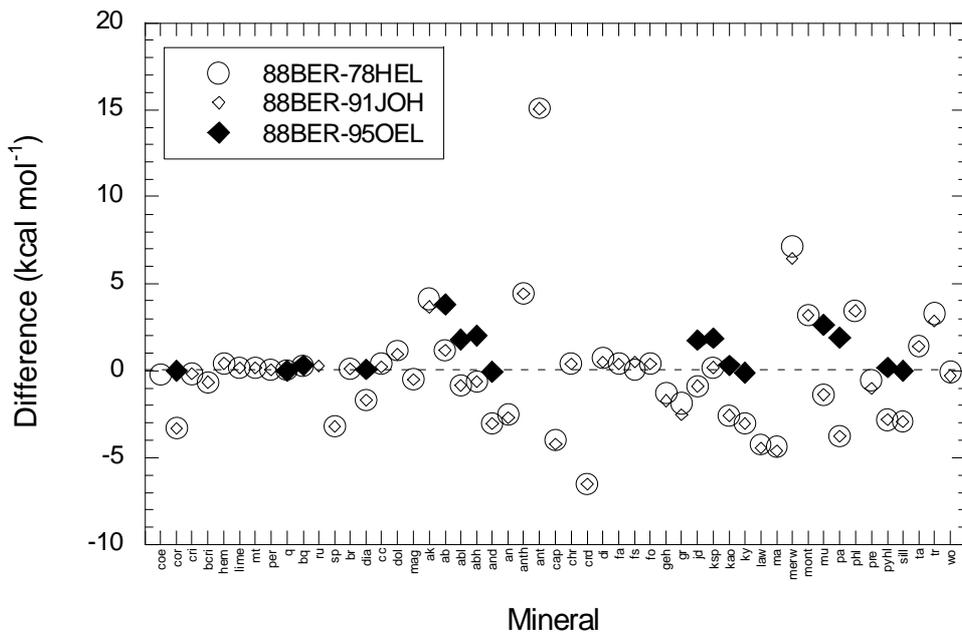
Figure 7. Differences in standard Gibbs free energies of formation of minerals between the 88BER and 78HEL, 91JOH and 95OEL databases.

A notation in the figures, such as 90HOL - 78HEL, signifies that the indicated parameter in one database (*i.e.*, from Helgeson *et al.*, 1978) is subtracted from that of another (*i.e.*, Holland and Powell, 1990).

Differences among standard molal volumes from Holland and Powell (1990) and those determined by Helgeson *et al.* (1978), Johnson *et al.* (1992) and Berman (1988) are shown in Fig. 4. As can be seen, there is little discrepancy among these data. This is because molar volume data are calculated on the basis of X-ray cell refinements, which are routinely determined with small standard errors, in the range of 0.1-0.2%. Molar volumes in the 91JOH database for celadonite, cummingtonite, glaucophane, grunerite, merwinite, and nepheline differ significantly compared with corresponding values in the 90HOL and 88BER databases, however.

A plot similar to Fig. 4 is shown for standard entropies in Fig. 5, where it can be seen that the entropies determined by Holland and Powell (1990) and Berman (1988) agree in most cases, but discrepancies exist for albite, clinochlore, cordierite, gehlenite and phlogopite. Berman (1988) assigns entropy values for "high" albite to albite, whereas Holland and Powell (1990), Helgeson *et al.* (1978) and Johnson *et al.* (1992), attribute values for "low" albite to this phase. Significant discrepancies (*e.g.*, greater than $\pm$ 2 cal K^{-1} mol^{-1}) exist between the 90HOL and 78HEL and 91JOH databases for ferrous dolomite, siderite, acmite (aegerine), almandine, andradite, annite, celadonite, edenite, epidote, gehlenite, glaucophane, nepheline, pargasite and prehnite.

A plot similar to Fig. 4 is shown for standard enthalpies in Fig. 6. The 90HOL and 88BER data agree reasonably well, but data for albite, high albite, clinochlore, cordierite, and meionite differ significantly (*e.g.*, greater than $\pm$ 2 kcal mol^{-1}). The discrepancy for albite may be more apparent than real for reasons noted above. A number of such discrepancies also exist between the 90HOL and 78HEL and 91JOH databases, *i.e.*, for corundum, spinel, akermanite, high albite, andalusite, andradite, anorthite, anthophyllite, clinozoisite, cordierite, grossular, jadeite, kalsilite, kyanite, lawsonite, margarite, merwinite, monticellite, muscovite, nepheline, paragonite, phlogopite, pyrophyllite, sillimanite and tremolite. Many of these minerals are aluminous phases, and the discrepancies could therefore reflect a systematic error in the 78HEL and 91JOH databases.

Differences among standard Gibbs free energies of formation retrieved by Berman (1988) and those retrieved by Helgeson *et al.* (1978) and Johnson *et al.* (1992) are shown in Fig. 7 (the 90HOL database does not include free energy values). Data from Oelkers *et al.* (1995), which include several revisions to the 78HEL database, are also shown in the figure for comparison. Significant discrepancies (*e.g.*, exceeding $\pm$ 2 kcal mol^{-1}) are apparent between the 88BER and 78HEL and 91JOH databases for corundum, spinel, akermanite, andalusite, anorthite, anthophyllite, Ca-Al pyroxene, cordierite, grossular, kaolinite, kyanite, lawsonite, margarite, merwinite, monticellite, paragonite, phlogopite, pyrophyllite, sillimanite and tremolite. Revisions incorporated into the 95OEL database, however, agree substantially better with the 88BER data. This improvement includes revised data for corundum, diaspore, andalusite, kaolinite, kyanite, paragonite, pyrophyllite and sillimanite. Moreover, major discrepancies ($> \pm$ 2 kcal mol^{-1}) remain only for albite and muscovite. The discrepancy involving albite is probably due to differences between the 88BER and other databases in assigning the properties of either low, or high, albite to albite.

Figures 4 – 7 reveal generally good agreement among all the databases with regard to standard molal volumes and entropies, but rather poor agreement with regard to standard enthalpies and Gibbs free energies of formation. All the databases are internally consistent and are constrained by similar, and in some cases identical, calorimetric and phase-equilibrium data. Discrepant values must therefore result from differences in the respective definitions of internal consistency, including differences in calorimetric reference data, and/or differences and associated uncertainties in mathematical functions used to extrapolate high-temperature, high-pressure experimental data to the much lower reference pressure and temperature (Engi, 1992). The comparisons shown in Figs. 4 - 7 demonstrate that although thermodynamic functions calculated using two or more internally consistent databases may closely agree with each other and with the available experimental data, the corresponding standard-state properties of minerals, gases and aqueous species used in the calculations may differ significantly depending on differences in the choices made to define internal consistency.

4.2   Consistency versus completeness

A thermodynamic database developed for use in safety assessments must be relevant to the system of interest, *i.e.*, the system of engineered and natural barriers that will evolve over long periods of time in response to both internal and external features, events and processes. A reliable thermodynamic database should therefore include data for all aqueous species, gases and solid phases that are important in such systems. If these data are not included, then their absence may diminish the reliability of a database more severely than any deficiencies in its level of internal consistency.

The question of completeness also extends to whether conditions that are not relevant to the system of interest should be represented in a database. Nordstrom *et al.* (1990), for example, make the reasonable argument that because reversible solubilities for many minerals have never been convincingly demonstrated at low temperatures and pressures, equilibrium constants for these reactions should not be included in a thermodynamic database appropriate for such conditions. An alternative view is that such considerations should be exercised when the data are applied to a particular problem, not when the database itself is being developed. This is because there is always some level of interdependence among thermodynamic data, and valuable constraints on the thermodynamic properties of minerals that exhibit reversible equilibrium at low temperatures, for example, can therefore be extracted from the results of high-temperature and high-pressure experiments involving minerals that do not exhibit such behavior. This suggests that a thermodynamic database supporting safety assessments should be complete in two senses: 1) that it contains data for all minerals, gases and aqueous species that are important in the repository system, and 2) that it contains similar data for other minerals, gases and aqueous species that may not be relevant to the repository system, but which can be used to help constrain data that are.

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Appendix 1: SUPCRT Model and Databases

Databases that closely adhere to the concept of thermodynamic consistency given in Section 2 for minerals, gases and aqueous species, have evolved more-or-less continuously since 1974 through the combined efforts of researchers affiliated with the Laboratory of Theoretical Geochemistry at the University of California, Berkeley. For convenience, the results of this collective effort are referred to here as the SUPCRT[6] model, and its associated databases.

A1.1   The SUPCRT Model

The SUPCRT model includes:

- an equation of state for H_2O (Levelt-Sengers *et al.*, 1983; Haar *et al.*, 1984),

- equations enabling calculation of the dielectric properties of the solvent as functions of temperature and pressure (Johnson and Norton, 1991),

- the revised HKF (Helgeson-Kirkham-Flowers; Helgeson *et al.*, 1981) equations of state for aqueous species, and equations to calculate their apparent standard partial molal thermodynamic properties as functions of temperature and pressure (Tanger and Helgeson, 1988), and

- equations of state for minerals and gases, and equations to calculate their apparent standard molal thermodynamic properties as functions of temperature and pressure (Helgeson *et al.*, 1978).

The thermodynamic framework represented by these equations as a whole, and their temperature, pressure and solvent density (ρ_{H2O}) regions of validity, is described by Helgeson and Kirkham, 1974a,b; Helgeson and Kirkham, 1976; Helgeson *et al.*, 1978; Helgeson *et al.*, 1981; Shock and Helgeson, 1988; Tanger and Helgeson, 1988; Johnson *et al.*, 1992; Shock *et al.*, 1992; Sassani and Shock, 1992; Shock and Koretsky, 1995; Haas *et al.*, 1995; Shock *et al.*, 1997a,b; Sverjensky *et al.*, 1997). The SUPCRT model permits calculation of the apparent standard molal thermodynamic properties of minerals and gases from 1 to 10000 bars and from 0°C to a maximum value consistent with the Maier-Kelly (Maier and Kelly, 1932) heat-capacity coefficients for the mineral or gas of interest. For charged aqueous species, calculation of the apparent standard partial molal Gibbs free energy of formation is restricted to $\rho_{H2O} > 0.35$ g-cm^3, and to $T \leq 350$°C, or $T \geq 400$°C at $P < 500$ bars. Calculation of the standard partial molal enthalpy of formation of charged species and their standard partial molal entropy, heat capacity and volume is limited to $\rho_{H2O} \geq 0.35$ g-cm^3 and $T \leq 350$°C at $P < 1000$ bars.

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[6] SUPCRT is an abbreviation of "supercritical".

The standard state adopted in the SUPCRT model for thermodynamic components that are stoichiometrically equivalent to minerals calls for unit activity of the pure component at any pressure and temperature. For liquids, including $H_2O(l)$, the standard state corresponds to unit activity of the pure solvent at any pressure and temperature. The standard state for gases is unit fugacity of the hypothetical ideal gas at 1 bar and any temperature. For aqueous species other than H_2O, the standard state is unit activity in a hypothetical ideal one molal solution referenced to infinite dilution at any pressure and temperature.

Standard molal Gibbs free energies and enthalpies of formation of minerals, gases and aqueous species are calculated in the SUPCRT model in terms of their apparent standard molal counterparts[7]. The apparent standard molal Gibbs free energy and enthalpy of formation ($\Delta G^{\circ}_{P,T}$ and $\Delta H^{\circ}_{P,T}$ respectively) are defined at a given pressure and temperature by:

$$\Delta G^{\circ}_{P,T} \equiv \Delta G^{\circ}_{f} + \left(G^{\circ}_{P,T} - G^{\circ}_{Pr,Tr} \right),$$ (A1.1)

and

$$\Delta H^{\circ}_{P,T} = \Delta H^{\circ}_{f} + \left(H^{\circ}_{P,T} - H^{\circ}_{Pr,Tr} \right),$$ (A1.2)

where ΔG^{o}_{f} and ΔH^{o}_{f} represent the standard molal Gibbs free energy and enthalpy of formation from the elements in their stable phase at the reference pressure ($P_r = 1$ bar) and temperature ($T_r = 25°C$). The parenthetical terms in these equations refer to differences in the absolute standard Gibbs free energy ($G°$) and absolute standard enthalpy ($H°$) caused by changes in pressure ($P - P_r$) and temperature ($T - T_r$).

The parenthetical terms in Eqns. (A1.1) and (A1.2) are evaluated using equations-of-state for gases, minerals and aqueous species described by Helgeson and Kirkham (1974a,b), Helgeson *et al.*, (1981), Tanger and Helgeson (1988) and Johnson *et al.* (1992). The resultant equations (*e.g.*, Johnson *et al.*, 1992) for calculation of the thermodynamic properties of gases, minerals, aqueous species and reactions as a function of pressure and temperature are parameterized in terms of the corresponding standard molal and partial molal quantities, and temperature and pressure independent equation-of-state coefficients. These parameters are included in thermodynamic databases (see below) supporting calculations using the SUPCRT model. For gases and minerals that do not undergo phase transitions, these parameters include:

- ΔG°_{f},
- ΔH°_{f},
- $S^{\circ}_{Pr,Tr}$,
- $V^{\circ}_{Pr,Tr}$
- a_i, b_i, c_i, and

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[7] Apparent standard molal quantities are defined as a matter of convenience to avoid the necessity of accounting for changes in the stable phase of the elements with changes in temperature and pressure (*e.g.*, Anderson and Crerar, 1993). It is unnecessary to account for these changes because the thermodynamic properties of the elements always cancel in any balanced chemical reaction.

- T_{max},

where $S^o_{Pr,Tr}$ and $V^o_{Pr,Tr}$ refer to the standard molal entropy and volume, respectively, at the reference temperature and pressure, a_i, b_i and c_i denote pressure and temperature independent coefficients that are consistent with the Maier-Kelley equation describing the temperature dependence of the heat capacity, and T_{max} stands for the upper temperature limit of validity of these coefficients. These data are also required for minerals that experience phase transitions, in addition to the enthalpy and volume change at each transition temperature, and Maier-Kelly coefficients for each transitional phase and the upper temperature limits of their validity. For aqueous ions and neutral species, parameters appearing in thermodynamic databases supporting the SUPCRT model include:

- $\Delta \overline{G}^{\circ}_f$,
- $\Delta \overline{H}^{\circ}_f$,
- $\overline{S}^{\circ}_{Pr,Tr}$,
- a_1, a_2, a_3, a_4,
- c_1, c_2,
- $\varpi_{Pr,Tr}$, and
- Z,

where the first two parameters refer to the standard partial molal Gibbs free energy and enthalpy of formation, respectively, $S^o_{Pr,Tr}$ denotes the standard partial molal entropy, $a_{1...4}$ and c_1 and c_2 stand for pressure and temperature independent coefficients appearing in the revised Helgeson, Kirkham and Flowers (HKF) equation of state, $\omega_{Pr,Tr}$ represents the conventional Born coefficient, and Z refers to charge. The units of thermodynamic quantities in the SUPCRT model are temperature in Kelvins (°K), pressure in bars, energy in calories (cal), mass in moles (mol) and volume in cubic centimeters (cm^3).

A1.2   SUPCRT databases

Helgeson *et al.* (1978) first developed an internally consistent thermodynamic database compatible with the SUPCRT model. It was developed primarily on the basis of calorimetric and phase-equilibrium experimental data, and includes standard thermodynamic properties for 83 minerals in the system Na$_2$O-K$_2$O-CaO-MgO-FeO-Fe$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-TiO$_2$-H$_2$O-CO$_2$. This study also pioneered the use of equations-of-state for aqueous species [Na$^+$, K$^+$, O$_2$(*aq*) and SiO$_2$(*aq*); Helgeson and Kirkham (1974 a,b; 1976); Walther and Helgeson (1977)] to retrieve Gibbs free energies of formation of minerals from the results of solubility and mineral-stability experiments. The accuracy of the data is verified for more than 130 reactions in the form of diagrams, where experimental solution compositions, or phase-equilibrium reversal temperatures are compared with calculated equilibrium constants, or univariant/divariant equilibrium curves.

Johnson *et al.* (1992) utilized improvements to theoretical models giving more accurate representation of the thermodynamic and dielectric properties of H$_2$O at subcritical and supercritical temperatures and pressures to add data for 294 aqueous species, and an

additional 96 minerals, to the original Helgeson *et al.* (1978) database. The revised database is referred to as SPRONS92.DAT, and is included in the SUPCRT software package described by Johnson *et al.* (1992). Although the data for minerals are mostly from Helgeson *et al.* (1978), additional data for Sn-bearing minerals (Jackson and Helgeson, 1985), and a small amount of calorimetric data for other minerals are also included in SPRONS92.DAT. Johnson *et al.* (1992) correct the standard Gibbs free energies of formation of calcite and aragonite retrieved by Helgeson *et al.* (1978) using experimental solubilities for these minerals determined by Plummer and Busenberg (1982). The Gibbs free energies and enthalpies of several other Ca-bearing minerals evaluated by Helgeson *et al.* (1978), including anorthite, clinozoisite, diopside, dolomite, epidote, laumontite, wairakite, wollastonite, lawsonite, and margarite, are adjusted to be consistent with the revised data for calcite and aragonite. Thermodynamic data and equation-of-state coefficients for aqueous ions and ionic species are from Shock and Helgeson (1988). Similar data for inorganic neutral species are from Shock *et al.* (1989). Data for 86 organic species are also included in SPRONS92.DAT.

Oelkers *et al.* (1995) discuss results of calculations using SUPCRT and a modified version of SPRONS92.DAT, which includes revisions to thermodynamic data for minerals and aqueous species in the system Al_2O_3-H_2O-NaCl (Pokrovskii and Helgeson, 1995), and unpublished revisions to data for minerals and aqueous species in the system Na_2O-Al_2O_3-SiO_2-HCl. Standard Gibbs free energies of formation are the only data documented by these authors, however, (the complete database will be described in a future report; E. H. Oelkers, *pers. comm.).*

Arthur *et al.* (1999) developed an updated and revised version of SPRONS92.DAT that incorporates the results of laboratory and other relevant studies published in the scientific literature since 1991. Sources of the revised and updated data are described in the following paragraphs.

Pokrovskii and Helgeson (1995) evaluate experimental solubilities reported in the literature for gibbsite, boehmite, diaspore and corundum to derive an internally consistent set of thermodynamic data for Al^{3+}, $Al(OH)_2^+$, $Al(OH)_3(aq)$ and $Al(OH)_4^-$, and to retrieve standard molal Gibbs free energies of formation of boehmite and diaspore at the reference pressure and temperature. All available calorimetric, phase-equilibrium, solubility and potentiometric experimental data pertinent to the Al_2O_3-H_2O-NaCl system are considered in this study over a wide range of pressures and temperatures, and the retrieved data for this chemical subsystem are internally consistent. Standard molal thermodynamic properties and Maier-Kelley heat capacity coefficients for corundum, gibbsite, boehmite and diaspore retrieved by Pokrovskii and Helgeson (1995) are included in the database developed by Arthur *et al.* (1999). Standard partial molal thermodynamic properties and HKF equation-of-state coefficients for the aqueous aluminum species noted above, and for $NaAlO_2(aq)$ and $NaOH(aq)$, are also included. These internally consistent data are also consistent with data for Na^+, Cl^- and OH^- from Shock and Helgeson (1988) and data for $NaCl(aq)$ from Shock *et al.* (1989).

Shock *et al.* (1997a) use correlations among experimentally determined standard partial molal volumes, heat capacities and entropies to estimate standard partial molal properties and HKF equation-of-state parameters for more than 300 inorganic cations and anions, polyatomic anions, oxyanions, acid oxyanions, neutral oxy-acid species, dissolved gases

and hydroxide complexes of metal cations. In addition to these new data, revised data for 80 species from Shock and Helgeson (1988) are also provided. These revisions are motivated by improvements to previous correlations (Sassani and Shock, 1992; 1994). The revised correlations account for the coordination of aqueous ions, and associated effects on estimates of effective ionic radii and partial molal entropies (see also Puigdomènech et al., 1997).

Sverjensky et al. (1997) regressed experimental ion-association data reported in the literature to retrieve standard partial molal properties and HKF equation-of-state coefficients for 57 aqueous metal complexes with halogen (Cl^-, F^-, Br^-, I^-), carbonate, sulfate, nitrate, acetate, and $H_3SiO_4^-$ ligands. Correlations developed on the basis of experimental standard partial molal heat capacities, volumes and entropies of association, combined with similar data from Shock and Helgeson (1988) for aqueous cations and anionic ligands, are used to calculate provisional estimates of standard partial molal properties and equation-of-state coefficients for an additional 52 complexes, for which little or no experimental data are available.

Pokrovskii and Helgeson (1997a) regressed experimental dissociation constants reported in the literature to retrieve standard partial molal properties and HKF equation-of-state parameters for $KCl(aq)$. The retrieval strategy used data from Shock and Helgeson (1988) for the corresponding properties of K^+ and Cl^-.

Pokrovskii and Helgeson (1997b) regressed experimental data on the solubilities of gibbsite and corundum in aqueous KOH solutions to retrieve standard partial molal properties and HKF equation-of-state coefficients for $KAlO_2(aq)$ and $KOH(aq)$. These data are consistent with the thermodynamic properties of K^+ and OH^- retrieved by Shock and Helgeson (1988), and with the revised properties of AlO_2^- from Pokrovskii and Helgeson (1995).

Haas et al. (1995) used experimental data from the literature and correlation algorithms to retrieve or estimate standard partial molal thermodynamic properties and HKF equation-of-state parameters for 246 inorganic aqueous lanthanide complexes with halogen (Cl-, F-), hydroxide, carbonate, sulfate, bicarbonate, nitrate and orthophosphate ligands. The retrieval and estimation procedures are constrained by data from Shock and Helgeson (1988).

Shock and Koretsky (1995) regressed experimental equilibrium constants for association of metal-organic complexes involving monovalent organic acid ligands to retrieve, or estimate, standard partial molal thermodynamic properties and HKF equation-of-state coefficients for 270 metal-organic species. The organic ligands and associated acids include formate, acetate, propanoate, butanoate, pentanoate, glycolate, lactate, oxalate and succinate. Data for 114 metal acetate complexes from Shock and Koretsky (1993) are consistent with the Shock and Koretsky (1995) data for the corresponding organic ligands.

Saccocia and Seyfried (1993) reinterpreted published experimental phase-equilibrium data involving chamosite (synonymous according these authors with 14Å-daphnite) and retrieved values of the standard molal Gibbs free energy and enthalpy of formation for 14Å-daphnite. These revised data are consistent with the standard entropy, volume and Maier-Kelley heat capacity coefficients for 14Å-daphnite from Helgeson et al. (1978).

Sverjensky *et al.* (1991) reconciled inconsistencies in the thermodynamic properties of minerals in the systems K_2O- and Na_2O-Al_2O_3-SiO_2-H_2O-HCl using an analysis procedure that integrates the results of phase-equilibrium and calorimetric experiments with the results of solubility experiments at high temperatures. Values reported by Helgeson *et al.* (1978) for the Gibbs free energy of formation of muscovite, phlogopite, K-feldspar, sanidine and microcline are revised accordingly. Sverjensky *et al.* (1991) also retrieved standard partial molal thermodynamic properties and HKF equation-of-state coefficients for HCl(*aq*). More recent data for this species from Tagirov *et al.* (1997) [see below] are, however, compatible with all experimentally determined dissociation constants for HCl(*aq*) over a wider range of temperatures, pressures and H_2O densities than were considered by Sverjensky *et al.*(1991).

Oelkers *et al.* (1995) determined standard partial molal thermodynamic properties and HKF equation-of-state coefficients for two aluminum acetate complexes [$Al(CH_3COO)^{2+}$ and $Al(CH_3COO)^{2+}$]. These data are consistent with the revised data for Al^{3+} from Pokrovskii and Helgeson (1995).

Shock *et al.* (1997b) use the available experimental data from the literature to estimate HKF equation-of-state parameters for aqueous uranium cations and hydroxide complexes , and to retrieve standard molal thermodynamic properties and Maier-Kelley heat capacity coefficients for uraninite. These data are consistent with thermodynamic properties reported by Grenthe *et al.* (1992) and experimental uraninite solubilities at high temperatures determined by Parks and Pohl (1988).

Standard partial molal thermodynamic properties and HKF equation-of-state coefficients for Pd^{2+}, $PdCl^+$, $PdCl_2$(*aq*), $PdCl_3^-$, $PdCl_4^{2-}$, $Pd(OH)^+$ and PdO(*aq*) are estimated by Sassani and Shock (1990) using the limited available experimental data on dissociation constants from Droll *et al.* (1957), Biryukov and Shlenskaya (1964) and Izatt *et al.* (1967). Standard molal thermodynamic properties and Maier-Kelley heat capacity coefficients for Pd(*c*) and PdO(*c*) are also determined.

Standard partial molal thermodynamic properties and HKF equation-of-state parameters for the ion-pairs $NaB(OH)_4$(*aq*) and $NaSO_4^-$ are retrieved by Pokrovski *et al.* (1995) from potentiometric measurements of the respective association constants between 50 and 200°C. The data are consistent with thermodynamic properties and HKF equation-of-state parameters for Na^+, OH^- and SO_4^{2-} from Shock and Helgeson (1988) and Shock *et al.* (1997a).

Tagirov *et al.* (1997) retrieved standard partial molal thermodynamic properties and HKF equation-of-state coefficients for HCl(*aq*) based on association constants consistent with measured solubilities of AgCl(*c*) and Ag(*c*). The experimental data determined in this study are evaluated simultaneously with association constants retrieved from other solubility and electrical conductance measurements reported in the literature between 25 and 700°C, and between 1 bar and 5 kb. Standard partial molal properties and HKF parameters for $AgCl_2^-$ were also determined by Tagirov *et al.* (1997). The data for both HCl(*aq*) and $AgCl_2^-$ are consistent with the thermodynamic properties and HKF equation-of-state coefficients for Cl^- from Shock and Helgeson (1988) [which are unrevised by Shock *et al.* (1997a)], and thermodynamic properties and Maier-Kelley coefficients for AlCl(*c*) (chlorargyrite) and Ag(*c*) from Helgeson *et al.* (1978).

Appendix 2: The OECD/NEA Databases

The Radioactive Waste Management Committee (RWMC) of the Organisation for Economic Cooperation and Development (OECD) Nuclear Energy Agency (NEA) established the NEA Thermochemical Data Base (TDB) project to develop an internationally accepted thermochemical database specifically for radioelements considered in safety assessments of geologic repositories for nuclear wastes (Östhols and Wanner, 2000). The project's aims are to produce a database that:

- contains data for all the elements of interest to radioactive waste disposal,
- documents how and why the data were selected,
- gives recommendations based on original experimental data, rather than compilations and estimates,
- documents the sources of experimental data used,
- is internally consistent, and
- treats all solids and aqueous species of the elements considered in nuclear waste performance assessment models.

Databases developed by the OECD/NEA TDB project are standard sources of high-quality, internally consistent thermodynamic data. The reliability of these databases can be attributed to the project's rigorous adherence to a set of well documented procedures for data selection (Wanner and Östhols, 2000), for carrying out ionic-strength corrections (Grenthe *et al.,* 1997) and temperature corrections (Puigdomènech *et al*., 1999), for dealing with uncertainties in experimental data and assigning uncertainties to retrieved thermodynamic parameters (Wanner and Östhols, 1999), and for other more routine matters of data handling (Östhols and Wanner, 2000).

The OECD/NEA TDB project adopts a standard-state definition consistent with that specified by the International Union of Pure and Applied Chemistry (IUPAC) [Laffitte, 1982]. For pure substances and mixtures, the standard state is defined as follows:

- for a gaseous substance, whether pure or in a gaseous mixture, the standard state is the pure substance and the standard-state pressure and in a (hypothetical) state in which it exhibits ideal gas behavior,

- for a pure liquid, the standard state is the (ordinarily) pure liquid at the standard state pressure,

- for a pure solid, the standard state is the (ordinarily) pure solid at the standard state pressure, and,

- for a solute in solution, the standard state is a hypothetical ideal 1 molal solution of the solute at the standard state pressure.

The standard-state pressure is 0.1 MPa (1 bar). The standard-state temperature is unspecified, but a temperature of 298.15 °K (25 °C) is chosen as the reference temperature. The data set collected in the OECD/NEA TDB project include for stoichiometric solids,

gases and aqueous species the standard molar Gibbs energy and enthalpy of formation, the standard molar entropy, and the standard molar heat capacity at constant pressure and associated coefficients used in an empirical equation to describe its temperature dependence. Thermodynamic functions calculated from these parameters are also included for selected reactions. The units of thermochemical parameters in the NEA TDB project follow the *Système International d'unité* (SI units). The unit of energy is the joule.

A2.1   OECD/NEA Databases

Thermodynamic databases have been developed by the OECD/NEA TDB project for inorganic compounds of U (Grenthe *et al.,* 1992), Am (Silva *et al.,* 1995), Tc (Rard *et al.,* 1999), and Np and Pu (Lemire, 2001). New reviews and additional database development planned in Phase II of this project include (Östhols and Wanner, 2000):

- an update of U/Am/Tc/Np/Pu databases,
- inorganic complexes and compounds of Ni
- inorganic complexes and compounds of Se,
- simple organic ligands (isosaccharinic acid, EDTA, citrate and oxalate) of U, Am, Tc, Np, Pu, Ni, Se, Zr and some competing cations, and
- inorganic complexes and compounds of Zr.