Where to find equilibrium constants?

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Abstract

A crucial part of any equilibrium modelling calculation is the selection of equilibrium constants that quantify the strength of interactions between metals and ligands. For researchers new to the field of solution chemistry, locating suitable equilibrium constants that lead to reliable model results can be problematic. Numerous large compilations of equilibrium constant values have been published each having their own limitations, coverage and availability. This work surveys twelve major compilations of equilibrium constants including those from authoritative groups such as IUPAC, NIST, and NEA. For each compilation surveyed, details are given related to the historical background and underlying project, scope of the database with respect to range of included metals and ligands, and the present-day availability of publications or computer databases resulting from the project. The various methods employed by different data compilers in their critical assessment for each compilation are also discussed.

1. Introduction

Understanding the chemical behaviour of aqueous solutions is an important aspect in many fields, ranging from the environment to toxicology to regulatory. Workers in these and other fields may gain insight into various problems by analysing the results of equilibrium modelling calculations containing the metals and ligands of interest to them. An essential component of any equilibrium model is the set of thermodynamic equilibrium constants appearing in the calculations. One of the effects of the progressive loss of expertise in %   %% f %   %   % % f   %   , do not know where to find the right constants to use in their models. Often the approach taken is either to blindly use one of many available calculation packages (without considering the validity of the constants included), or to google for equilibrium constants applicable to the problem at hand. A more sensible and efficient approach would be to check whether the required values exist in equilibrium constant compilations. However, which compilations exist, how to access them, what they cover, etc. is largely unknown by newcomers to the field.

This paper intends to shed light on compilations of equilibrium constants, giving some historical background of major compilations, outlining the scope of the data within, and commenting on the present availability of publications and / or databases containing the equilibrium constants. It is provided primarily for lay people and focuses mainly on ambient temperature at 1 atm pressure.

This work surveys both critical and non-critical compilations of equilibrium constants. Non-critical compilations tend to provide a more comprehensive picture of the available data than their critical counterparts, which tend to be focussed on, for instance, the chemistry of particular metals and/or ligands. №%%   f %   % %   % f %   f can mean very different things: some critical compilations detail any single reason why a given value is

acceptable or not and, sometimes, but not f f l% %f%g %f l while others just give values without clearly explaining the choices behind their selection. In some cases, the justifications behind data selection were envisioned to be published but never eventuated.

This paper does not deal with other parameters needed to perform calculations in real multicomponent media such as those related to activity coefficients or temperature corrections. These are also obscure fields for many users but the subject will be dealt with in another paper.

2. Brief reminder on equilibrium constants and related thermodynamic quantities

Selected equilibrium constants in critical compilations usually refer to the reference temperature $T° = 298.15$ K (25°C) and to the standard state, i.e. a pressure of 0.1 MPa (1 bar) and, for aqueous species, infinite dilution (ionic strength $I = 0$). For example, for the reaction

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3(aq) \tag{1}$$

the equilibrium constant at the reference temperature and for the standard state is defined as

$$\log_{10}K° = \log_{10} a(CaCO_3(aq)) \quad \log_{10} a(Ca^{2+}) \quad \log_{10} a(CO_3^{2-}) \tag{2}$$

where $a(X.$% % % f % f % %f % % %X (all species considered in this work are aqueous unless otherwise indicated). If $\log_{10}K$ does not refer to the reference temperature $T°$ and/or the standard state, this should be stated explicitly in the data compilation in order to avoid ambiguities.

This equilibrium can alternatively be described by its molar Gibbs free energy of reaction

$$\Delta_r G_m° = \Delta_f G_m°(CaCO_3(aq)) \quad \Delta_f G_m°(Ca^{2+}) \quad \Delta_f G_m°(CO_3^{2-}) \tag{3}$$

where $\Delta_f G_m°(X)$ [kJ·mol^{-1}] is the standard molar Gibbs free energy of formation of species X.

The relation between both quantities is

$$\Delta_r G_m^\circ = R \cdot T^\circ \cdot \ln K^\circ = R \cdot T^\circ \cdot \ln(10) \cdot \log_{10} K^\circ \tag{4}$$

where R [J·K^{-1}·mol^{-1}] is the molar gas constant.

Data compilations may either consist of $\log_{10} K^\circ$ values for reactions or $\Delta_f G_m^\circ$ [kJ·mol^{-1}] values for species, or combinations of both. Often in older compilations $\Delta_f G_m^\circ$ values are given in [kcal·mol^{-1}]; to convert from the thermochemical calorie (cal) to joule (J) the value given in (cal) has to be multiplied by 4.184 (exactly).

In some cases, data compilations, e.g. CODATA key values (Cox *et al.* 1989), consist of other fundamental thermodynamic quantities: $\Delta_f H_m^\circ$ [kJ·mol^{-1}], the standard molar enthalpy of formation, and S_m° [J·K^{-1}·mol^{-1}], the standard molar entropy. The Gibbs free energy of formation, e.g. $\Delta_f G_m^\circ(Ca^{2+})$ from the above example, is calculated from these quantities according to the Gibbs-Helmholtz equation:

$$\Delta_f G_m^\circ(Ca^{2+}) = \Delta_f H_m^\circ(Ca^{2+}) \quad T^\circ \cdot \Delta_f S_m^\circ(Ca^{2+}) \tag{5}$$

where $\Delta_f S_m^\circ(Ca^{2+})$ [J·K^{-1}·mol^{-1}] is the standard molar entropy of formation of Ca^{2+}, which in turn is calculated from the elements in their standard states according to the reaction

$$Ca(cr) + 2H^+ \rightleftharpoons Ca^{2+} + \tfrac{1}{2}H_2(g) \tag{6}$$

$$\Delta_f S_m^\circ(Ca^{2+}) = S_m^\circ(Ca^{2+}) + (1/2)\, S_m^\circ(H_2, g) \quad S_m^\circ(Ca, cr) \tag{7}$$

Note that $S_m^\circ(H^+) = 0$ by definition. Note further that some older gas data are given at 1 atm (1.01325 bar) in their original sources. The entropy values of gases are sensitive to pressure and have to be converted from 1 atm to 1 bar using the equation:

$$S_m°(\text{bar}) \quad S_m°(\text{atm}) = R \cdot \ln(1.01325/1.0) = 0.1094 \text{ J·K}^{-1}\cdot\text{mol}^{-1} \tag{8}$$

3. Non-critical IUPAC compilation

3.1 Historical

For many years, the International Union of Pure and Applied Chemistry (IUPAC) sponsored a non-critical compilation of metal complex equilibrium constants. The result was the publication of two small and four large volumes of stability constants. The initial volumes were edited by Bjerrum *et al*. (1957; 1958). The first major volume, edited by L.G. Sillén (for inorganic ligands) and A.E. Martell (for organic ligands), was published in 1964 (Sillén *et al*. 1964). The second volume, subtitled supplement No. 1, edited by L.G. Sillén and E. Högfeldt (for inorganic ligands) and A.E. Martell and R.M. Smith (for organic ligands), was published in 1971 and covered the literature through 1968 (Sillén *et al*. 1971). Further work by Perrin (1979) and Högfeldt (1982) produced two additional volumes of stability constants covering equilibria with organic and inorganic ligands that appeared in the literature up to 1974. The larger compilations attempted to include all papers in the field related to metal complex equilibria. In 1990, a computerised database containing the values from the IUPAC volumes was created by L. Pettit. The database   known as SC-Database   f %   g   %g %U   % company *Academic Software* and was kept up to date with new values from the literature with the help of an extended team.

3.2 Scope

The IUPAC volumes and SC-Database aimed to include all published constants with no assessment of their quality. Most of the papers published in the twentieth century that contained stability constants, enthalpies, entropies and free energies of metal complexes in both aqueous and non-aqueous media were compiled. In one of the later versions of the SC-

Database it was noted that fewer than 32 % of the data had originated with the IUPAC

% 3 ⅜g   % 9.% % f % % %755: % %65   55% cords for   755% f

%   %7 : 55%   %   %   f   % % %XH-Database. However Pettit and Pettit

(2009) would later write that:

 New stability constants reported in the literature are now, in general, not designed for

general use by other scientists. Rather, they are measured to confirm a reaction mechanism or

to identify bonding centers. The ligands studied are becoming more esoteric (e.g.,

calixarenes, or long-chain peptides), and the constants are often measured less rigorously and

to a lower precision than earlier measurements. As a result, the constants are frequently of

less general use and are less appropriate for inclusion in the IUPAC Stability Constants

Database. The abstraction and compilation of new literature data will, therefore, probably

cease during 2009 but the database will continue as an invaluable and irreplaceable resource,

which should be maintained and made available into the future. However, this has not been

the case (see below).

3.3 Availability

The IUPAC volumes may still be available in some science libraries but can also be obtained

at relatively low cost from online / second-hand bookstores.

The SC-Database was still being distributed by *Academic Software* until 2016-17 but is no

longer available from any source. Due to the age of the software, users with copies of the SC-

Database may face difficulties getting the program to run on modern computers.

4. Critical IUPAC publication of equilibrium data

4.1 Historical

In 1977 the Commission on Equilibrium Data of the Analytical Division of IUPAC (now IUPAC Solubility and Equilibrium Data Subcommittee) started to promote the writing of critical surveys of stability constants of metal complexes of specific ligands or small groups of related ligands. Each survey was prepared by experts working actively in the field of thermodynamics of complexes, and commented on by the members of the Commission on Equilibria Data.

As part of the critical assessment, data were classified in four categories: recommended, tentative, doubtful and rejected. According to the first IUPAC regulations, the data could be recommended (R) if the results of at least two independent research groups are in good agreement; if the surveyor has no doubt as to the adequacy of the applied experimental and calculation procedure; if the consideration of the activity concentration relation is correct, and the standard state is unambiguous. The given error of such a constant must be no less than ±0.05 logarithmic units. Data could be regarded as tentative (T) if all the conditions mentioned for R category are fulfilled, except the first one; or if the surveyor observes some deviation from the necessary rigorousness, but this probably caused no serious mistakes. The given error of such a constant must not exceed ±0.2 logarithmic units. Data should be considered as doubtful (D) if the surveyor suspects some errors in the evaluation of the constants, which are nevertheless of semi quantitative value. The probable error of such a constant should not exceed ±0.2 logarithmic units. Data determined by either an inadequate method, or under undefined conditions should be rejected (Rj). The same category is given if any serious objection is found in the evaluation.

More recently, criteria have been modified and literature data have been accepted as reliable - f % %% f %Xfg .1% % % %% % %f 1% % all, or in some cases most, of the following requirements have been met: (i) full experimental details are reported (solution stoichiometry, electrode calibration method, temperature, ionic strength, error analysis); (ii) the equilibrium model is considered to be complete (including hydrolysis reactions); (iii) data were measured in an essentially non-complexing medium; and (iv) the experimental method and numerical analysis are considered to have minimal systematic errors.

4.2 Scope

The list of published surveys can be found in Table 1. The most recent reviews (Powell *et al*. 2005, 2007, 2009, 2011, 2013) focus on the chemical speciation of the environmentally significant metals Hg, Cu, Pb, Cd and Zn in +II oxidation state (aerobic systems) with analysis limited to the inorganic ligands OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-}. The recent reviews have been prepared by the same group of experts scrutinising data reported in the SC-Database. Detailed discussions of the pros and cons of each decision in the selection of the recommended constants from the literature values are given in each report.

4.3 Availability

The critical reviews published in Pure & Applied Chemistry until 2013 can be downloaded for free. In 2014 the publishing rights for new reviews were obtained by De Gruyter (although no new reviews have appeared since that time) and therefore may attract a fee for access.

5. Critical IUPAC publication of solubility data

5.1 Historical

The IUPAC's Solubility Data Series (SDS), begun in the mid-1970s, is an exhaustive compilation and critical evaluation of all the world's published results of experimental determinations of solubility. It is not concerned chiefly with the assessment of equilibrium constants. However, solubility products and other equilibria are discussed depending on the chemical system in question so we include it here for completeness.

Since 1979, over 70 SDS volumes have been published, including evaluated data on the solubility of gases in liquids, liquids in liquids, and solids in liquids. Since 1998, and following an agreement with NIST, the SDS compilations have been published four times a year in the Journal of Physical and Chemical Reference Data. Since January 2002, a Subcommittee on Solubility and Equilibrium Data of the IUPAC Analytical Chemistry Division has continued the coordination of the SDS-related projects.

5.2 Scope

The IUPAC Solubility Data Project (SDP) has as its aim a comprehensive review of published data for solubilities of gases, liquids and solids in liquids or solids. A uniform format is followed for the assessment of all literature data sets. Where data from different sources agree sufficiently, recommended values are proposed. More information can be found at: https://srdata.nist.gov/solubility/intro.aspx. Table 2 lists all references of interest for the reader.

5.3 Availability

The list of all solubility volumes is available at: https://srdata.nist.gov/solubility/IUPAC/iupac.aspx. Volumes 66-102 are available at the Journal of Physical and Chemical Reference Data and thus at a cost. The original volumes were scanned by NIST into PDF files and digitized. Table of Contents are provided for Volumes 20-40, providing a description of the organization of each of the volumes. These volumes are available in sections.

6. NBS Tables

6.1 Historical

The National Bureau of Standards (NBS, now NIST, National Institute of Standards and Technology) published a large set of   %f   1% he NBS Tables of chemical   f   %   %   inorganic substances and for organic substances usually containing only one or two carbon atoms (Wagman *et al.* 1982).

The NBS Tables are the result of one of the widest-reaching and longest-running critical assessment tasks ever. Wagman *et al.* (1982) make the following statements about the work:

   X f f %   % %   % f %g % %   % % %f   % % % 3% % % list the measurements considered and those used, show how well the selected values reproduce the measurements, indicate corrections that were made, identify auxiliary data that were used, and give the bibliographic citation for each measurement. These reports are expected not only to document this book but also to provide a set of evaluated process data that can be used in future evaluations without repetition of all of the analysis we have to make. One such report has been prepared as an experiment, on the compounds of thorium (Wagman *et al.* 1977).

Unfortunately, none of these envisioned reports ever appeared. Consequently, values in the NBS tables cannot be traced back to experimental data, nor can any statement be made about the quality or even adequacy of an individual value.

6.2 Scope

Values for the Gibbs free energy of formation, $\Delta_f G_m°$, the standard molar enthalpy of formation, $\Delta_f H_m°$, and the standard molar entropy, $S_m°$, are given for gaseous, liquid, and crystalline substances, for solutions in water, and for mixed aqueous and organic solutions. Values are not given for alloys or other solid solutions, fused salts or for substances of undefined composition. Compounds of the transuranium elements are not included.

Wagman *et al* 3%6 =7.% %7; 555% f   % % %   f %   f   %   % %
69 855% g f   1%   % f f   % %f %   % %   %phases and at
different c   f   3% f   % %   f   %6 %7 =36: %8 %   f %   %67 =55%   1%
  %9 955%f   % % gg %   %6 %8 ; 55% %   3% f   f %*et al*. (1982) estimate
 f %,5 555%   %   %   % % %   % % %fg 1%6   % f %   %roduced
6=5 555%f   % %   %   % % %   f   % f   3

6.3 Availability

The values of the NBS tables are still in widespread use in thermodynamic databases. The original publication (Wagman *et al*. 1982), a supplement to the Journal of Physical and Chemical Reference Data, is now available online: https://www.nist.gov/srd/journal-physical-and-chemical-reference-data-monographs-or-supplements

7. CODATA

7.1 Historical

CODATA (Committee on Data for Science and Technology, http://www.codata.org/) had in the past several task groups work

Related Mixtures, (Garvin *et al*. 1987). They   % % %   f %Y %   % %   f %

thermodynamic data is intended as a first of many to be prepared as a cooperative, ongoing

international project by experts who are geographically separated, but in computer-to-

computer communications, and shf %   %f f% %f   f   f %   3

N%   % f   %Y %K   %Garvin *et al*. (1987)   ?%F %   1%   %   %f% % %

systematic procedures, a prototype product and a small core group. The core group intends to

continue to refine the procedures and to prepare additional tables. The rate at which further

    %   %   1%   1%   % % %   % %   f   %fo   3

Y   %   % %   f   %   f   %f   % f % %f 1%f % %   %fg   %

remained the first and last publication of the task group.

The task group did work on at least one further project in 1988 - 1990, some of which was

finally published as a journal article (Parker and Khodakovskii 1995) where the authors state:

 Y   %f   % %   %with the evaluation and selection of the thermochemical properties

of the aqueous ions Fe^{2+} and Fe^{3+} and with those related key compounds   f % % % %   %

network . The evaluation of the above mentioned species is part of a study of the

thermochemical properties of iron and some of its compounds, undertaken as part of a larger

international project of thermodynamic tables under the auspices of the CODATA Task

L   % %b   f %Y   f %Yfg 3

The work of Parker and Khodakovskii (1995) has later been used in the NEA TDB review of

iron. Part 1 of this NEA review, comprising 1082 pages of documentation, has been

published (Lemire et al. 2013), part 2 is still pending.

Task Group on Geothermodynamic Data   This Task Group was started in 1984 with the

goal of extending the CODATA work on accurate thermodynamic properties of simple, well-

defined chemical compounds to the more complex minerals encountered by geologists. Preliminary reports were issued but the resources were not available to produce a comprehensive database of mineral thermodynamics (Lide and Wood 2012).

Task Group on Thermodynamic Data for Key Chemical Substances – A successor to the Key Values for Thermodynamics Task Group which completed its work in 1989, having established the data for 36 elements, this Task Group aimed at preparing recommended data sets for another ten key elements. Approved in 1994, the Group prepared initial reports on barium and strontium, and their compounds, in preparation for producing recommended values in 1996. However, the death of the chairman in 1995, along with the evaporation of financial support for thermodynamics work both in Russia and the US, combined to effectively nullify the activity of this group (Lide and Wood 2012).

7.2 Scope

Values for the standard molar enthalpy of formation, $\Delta_f H_m°$ [kJ·mol^{-1}], and the standard molar entropy, $S_m°$ [J·K^{-1}·mol^{-1}], are tabulated in *CODATA Key Values for Thermodynamics* (Cox et al. 1989) for 151 gaseous, liquid, and crystalline substances, and for basic aqueous species.

7.3 Availability

The book *CODATA Key Values for Thermodynamics* (Cox *et al*. 1989) is still available. Furthermore, all CODATA key values, and the Gibbs free energy of formation values, $\Delta_f G_m°$, calculated therefrom, are included as auxiliary data in all NEA TDB volumes, e.g. Lemire *et al*. (2013), which are free for download: https://www.oecd-nea.org/dbtdb/info/publications/

8. NIST Critically Selected Stability Constants of Metal Complexes

8.1 Historical

Robert M. Smith and Arthur E. Martell produced six volumes of critical stability constants covering the literature through 1985 (Martell and Smith, 1974, 1976, 1982; Smith and Martell, 1975, 1977, 1989). Later, the contents of these volumes and more recent data were digitised leading to the NIST Critically Selected Stability Constants of Metal Complexes Database (NIST Standard Reference Database 46).

The criteria applied in the selection of the constants are discussed in Smith and Martell (1985). They are: adequate control and description of the experimental method (temperature, ionic strength, nature of supporting electrolyte, purity of the ligand, calibration, adequate definition of the equilibrium quotients), and reliability of the investigator. Values reported by only one investigator f   %   %   %   %%   % f   %%   g %   %f   ℨ%   % several values are in close agreement, the mean value is used and values showing considerable deviation from the majority are eliminated. Criteria applied in other cases (e.g., poor agreement and few results available, similar relative values but different absolute magnitude) are also described.

8.2 Scope

The NIST database contains in total 6 166 ligands and 112 559 lines of data (metal stability constants and related equilibrium constants). For a given system, values at the published temperature and ionic strength are given. Although a complete bibliography for each ligand is provided, the references are not linked to any particular stability constant. A search feature that would allow the retrieval of all data for a specific metal was planned but never implemented.

8.3 Availability

This database has been discontinued but the latest version (Version 8) can be downloaded from https://www.nist.gov/srd/nist46.

Data quality is reflected through a weight system with a scale ranging from 0 (wrong values) to 9 (most reliable constants). Weights are assigned by the database compiler and evolve over time as new data become available. Importantly, comments related to the weighting of data can be recorded in the database.

Consistency between thermodynamic parameters for the same reaction and for other equivalent linear combinations of reactions is evaluated by software and thermodynamically consistent equilibrium constants for modelling calculations are computed. An example of this type of assessment   f   % %   % f %5 555%   f %   %f %g   % g   % recently (May and Rowland, 2018). JESS is able to identify the effects of the many assumptions that are involved in achieving thermodynamic consistency.

9.3 Availability

Throughout its life JESS has targeted many computing platforms (such as VAX-VMS, Unix, MS-DOS and Linux) but the main distribution of JESS and its databases today is via software compatible with Windows. While the entirety of the thermodynamic database is freely available online (http://jess.murdoch.edu.au), the full software package grants users with powerful tools for database interrogation and modification (e.g. to insert new species, reactions or constants), modelling facilities and access to other databases including physicochemical properties and solubilities from the literature. Access to the full package is granted under license (a nominal fee applies to academic users).

10. NEA Chemical Thermodynamics Series

10.1 Historical

In 1986, the S   f %   %   %   .% % %T f f % %   %H -operation and Development (OECD) undertook the development of a critically evaluated chemical

thermodynamic database for a number of elements and ligands of interest to nuclear technology, in particular to the performance assessment of geological repositories for spent nuclear fuel and radioactive waste (https://www.oecd-nea.org/dbtdb/). The critical assessment procedure applies rigorous evaluation techniques such as a uniform method to treat ionic strength dependencies and uncertainties. Equilibrium constants are categorised as either (i)

%f   I%   %6 %   f   % % %Yfg % %   %f   % % %₈   %

and included in the NEA electronic database (see below), or (ii) datf%fg   %6 %   %   %

 f   f   % %f %   % f f   %   I%   %f %   f % % eochemical

modelling but are known with lower certainty than the recommended values.

10.2 Scope

Thirteen volumes of the Chemical Thermodynamics Series have been produced so far (Table 3)I% f   %   % f % 555%f   % %   f   . The recommended data refer to the standard state and to 25 °C; extensive discussions of the data analyses and review processes are made available in the interests of transparency. W f   % %f f%fg   % %   %

 f   f   , it is up to the user to read the documentation and to find the useful data.

10.3 Availability

All volumes in the series can be downloaded from the NEA website: https://www.oecd-nea.org/dbtdb/info/publications. Note that Bruno et al. (2007.%%6% f -of-the-f   %   % % solid solutions and does not contain any thermodynamic data.

A new interactive TDB electronic database is now available. Registration with the NEA is required in order to obtain access. The content of the e-TDB includes (a) all recommended thermodynamic data of the 12 Chemical Thermodynamic Series volumes, (b) a PHREEQC

formatted database file, ready to download and use, and (c) searchable information on all the bibliographic references that have been used in the TDB published material.

11. PSI/Nagra

11.1 Historical

The PSI/Nagra database originates from the need of a tailor-made thermodynamic database used in safety assessments for planned Swiss geological repositories for radioactive waste. The first data f % f % %f f % mainly CODATA key values and other, very well established data (Pearson and Berner 1991) f % f %f f %f f %f f % from other databases (Pearson *et al*. 1992). The first major update (Hummel *et al*. 2002) included the NEA TDB reviews on U, Np, Pu, Am and Tc and own reviews of Al. Eu, Ni, Pd, Sn, Th and Zr. The second update (Thoenen *et al*. 2014) included the NEA TDB reviews on Ni, Se and Th and own reviews concerning silicate compounds and complexes.

The data categories were redefined for the second update:

- Core Data: Well characterised aqueous species, minerals and gases of elements involved in almost any type of speciation calculation. These data have been carefully selected and are widely accepted in different fields of application. The core data basically comprise the CODATA key values (Cox *et al*. 1989) and some other values of similar quality and almost worldwide acceptance.

- Recommended Application Data: Well characterised aqueous species, minerals and gases of elements important in different fields of application. The recommended application data are of high quality and well established, but in contrast to the core data, which may not be revised in the foreseeable future, the recommended

application data originate from rather active fields of environmental sciences and may be revised and improved over time.

- Supplemental Data: Supplemental aqueous species and minerals are less well-characterised than those in the recommended application data. They comprise uncertain data, not selected in the NEA TDB and other reviews but discussed there as suitable for scoping calculations and qualitative modelling. Estimates are provided for important species where experimental data are missing or unreliable. These estimates are based on chemical analogues, linear free energy relationships or other estimation methods found reliable by the reviewers.

An ongoing third major update, to be published in 2020, will include the NEA TDB reviews on Sn, Fe and organic ligands, the environmentally important elements Hg, Cu, Pb, Cd and Zn based on IUPAC reviews (Powell *et al.* 2005, 2007, 2009, 2011, 2013), and reviews of Ti, Ag, Sm, Eu, Ho, Po, Ac, Pa and Cf.

11.2 Scope

The PSI/Nagra database relies to a large extent on the values recommended so far by the and IUPAC and in addition performs critical reviews of original experimental papers. The Nagra/PSI database exists in two formats, one of them consisting of equilibrium constants which can be used by conventional speciation modelling codes, the other consisting of SUPCRT-based Gibbs energies of formation of all contained chemical species. The latter has the advantage to be tailor-made for the use in Gibbs energy minimization (GEM) codes. GEM codes facilitate the calculation of multi-component systems and can thus be easily used to calculate chemical adsorption and to model solid solutions.

11.3 Availability

The documentations of all versions of the PSI/Nagra database, including data tables, can be downloaded from the Nagra website (https://www.nagra.ch/en). The documentation and the electronic versions of the latest update are available at the PSI website: https://www.psi.ch/les/database

12. ThermoChimie

12.1 Historical

ThermoChimie (https://www.thermochimie-tdb.com/) is a thermodynamic database created and developed by Andra, the French national radioactive waste management agency, over the last 10 years. Data acquisition is supported by an experimental program, in addition to active literature survey and the development of predictive models.

12.2 Scope

ThermoChimie addresses geochemical modelling and performance assessment tasks for French geological repositories for radioactive waste. The key criteria determining data included in the ThermoChimie database are self-consistency, exhaustiveness and traceability. Its domain of application is mainly within a pH range of 6 to 13, Eh of -0.5V to +0.5V and for temperatures below 80°C.

The database contains source references for each selected equilibrium constant. However, there is no detailed documentation concerning the selection process of individual equilibrium constants.

12.3 Availability

There is online access to the latest version of the database and to some general documentation via https://www.thermochimie-tdb.com/.

13. THEREDA

13.1 Historical

THEREDA (Thermodynamic Reference Database, https://www.thereda.de/en/) is a joint project collectively planned and executed since 2006 by German and Swiss research institutions which work in the field of final disposal of radioactive waste.

13.2 Scope

The THEREDA project is dedicated to the creation of a comprehensive, internally consistent thermodynamic reference database. It provides thermodynamic data (including equilibrium constants) and Pitzer interaction coefficients which in conjunction with suitable codes allow for the calculation of solubilities of radio-toxic and chemical-toxic elements in electrolyte solutions up to high concentrations. The database is used for the geochemical modelling of processes in the near- and far-field of different host rock types, which are envisaged as potential sites for final repositories in Germany.

13.3 Availability

Registered users have access (free of charge) to the different releases of the database and to all references, from which the released data sets were created, via https://www.thereda.de/en/.

14. Last remarks

The amount of work that is required to be invested into critical assessment tasks is immense and newcomers to the field of equilibrium modelling would be wise to make benefit from available compilations of data. On the other hand, the very meticulous work required for such analyses implies that very few systems are dealt with and most remain untouched. Smith and Martell (1985) were particularly critical on this point. Certain disciplines such as radioactive waste disposal still hold claim to a significant core of experts capable of performing critical assessment of equilibrium constants, which is reflected in the fact that most of the work during the past 30 years — NEA Chemical Thermodynamics Series, PSI/Nagra, ThermoChimie (Andra), THEREDA — is connected to the problem of nuclear waste management in some way. However, other fields are lacking the resources and skilled experts necessary to perform critical assessments and recommend equilibrium constants.

The persistence of existing compilations is problematic given that it is widely underappreciated how much ongoing work and effort are required just to maintain and distribute functional versions of computer databases. The IUPAC SC-Database is a pertinent example where lack of resources over a lengthy period means that one of the most comprehensive compilations of equilibrium constants is no longer officially distributed in any form. Although the latest version of the NIST Standard Reference Database 46 is still officially distributed, its persistence into the future is similarly doubtful given that its current use relies on the availability of backwards-compatible hardware and operating systems. If the field of nuclear waste management were to lose support, the future availability of many other long-standing compilations could also be jeopardised.

A further aspect to take into account is the difficulty of updating critical reviews to acknowledge new data that has appeared in the intervening years. This is a monumental task,

often proving to be prohibitive. In the case of the NBS Tables (Wagman *et al*., 1982), the

% % % in 1963 and would have been too costly to alter (even if

new information appeared in the literature) without affecting the analysis of nearly every

other f % % %f %% % % % % % % % %

f % % % % % % % % J F% % %N ?%The time required to carefully

compile and consider data dictates that any f fgf % % % f % % -of- f when it

appears in print %Q %*et al*., 2013). Owing to the difficulty of performing critical

assessment it is important to offer a warning here against modifying existing constants or

inserting new constants into databases. Done without expert care, this is likely to introduce

thermodynamic inconsistency that will make the results of equilibrium model calculations

spurious or even completely incorrect.

Acknowledgements

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Table 1.

Critical IUPAC equilibrium data

Ligand or system[a]	Reference
EDTA	Anderegg (1977)
1,10-P f 1%17 -bipyridyl and related compounds	McBryde (1978)
8-hydroxyquinoline	Starý et al. (1979)
Fluoride	Bond and Hefter (1980)
Acetylacetone	Starý and Lijenzin (1982)
NTA	Anderegg (1982)
Indium	Tuck (1983)
Histidine, phenylalanine, tyrosine, L-DOPA and tryptophan	Pettit (1984)
Ethylenediamine	Paoletti (1984)
Cyano complexes	Beck (1987)
Nucleotide complexes	Smith et al. (1991)
Glycine	Kiss et al. (1991)
Alanine, Valine, Leucine	Sovágó et al. (1993)
Cysteine, Cystine, Methionine, Serine, Threonine, Asparagine, Glutamine	Berthon (1995)
Agrinine, Lysine, Ornithine	Yamauchi and Odani (1996)
Salicylic acid and other aromatic hydroxycarboxylic acids	Lajunen et al. (1997)
Phosphonic acids	opov et al. (2001)
Crown ethers	Arnaud-Neu et al. (2003)
Aliphatic hydroxo-acids	Portanova et al. (2003)
IDA, MIDA, DTPA, TTHA, DOTA, NOTA, TETA	Anderegg et al. (2005)
Hg^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}	Powell et al. (2005)
Cu^{2+} + OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}	Powell et al. (2007)

Pb^{2+} + OH⁻, Cl⁻, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}	Powell *et al.* (2009)
Cd^{2+} + OH⁻, Cl⁻, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}	Powell *et al.* (2011)
Zn^{2+} + OH⁻, Cl⁻, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}	Powell *et al.* (2013)

[a]Abbreviations: MIDA - Methyliminodiacetic acid; TTHA - Triethylenetetraminehexaacetic acid; NOTA - 1,4,7-Triazacyclononane-N,N',N''-triacetic acid; TETA -Triethylenetetramine; DOTA - 1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid.

Table 2.

Critical IUPAC solubility data

System	Reference
Scandium, yttrium, lanthanum and lanthanide nitrates	Siekierski *et al*. (1983)
Alkaline earth metal halates	Miyamoto *et al*. (1983)
Copper, silver, gold and zinc, cadmium, mercury oxides and hydroxides	Dirkse (1986)
Sulfites, selenites and tellurites	Masson *et al*. (1986)
Alkali metal orthophosphates	Eysseltova and Dirkse (1988)
Hydrogen sulfide, deuterium sulfide and hydrogen selenide	Fogg and Young (1988)
Copper and silver halates	Miyamoto *et al*. (1990)
Alkaline earth hydroxides in water and aqueous solutions	Lambert and Clever (1992)
Copper(I) halides and pseudohalides	Fritz and Koenigsberger (1996)
Ammonium phosphates	Eysseltova and Dirkse (1998)
Solubility of inorganic actinide compounds	Hala and Miyamoto (2007)
Rare earth metal chlorides in water and aqueous systems. Part 1. Scandium group (Sc, Y, La)	Mioduski *et al*. (2008)
Rare earth metal chlorides in water and aqueous systems. Part 2. Light lanthanides (Ce-Eu)	Mioduskia *et al*. (2009
Rare earth metal chlorides in water and aqueous systems. Part 3. Heavy lanthanides (Gd-Lu)	Mioduski *et al*. (2009)
Alkali metal nitrates. Part 1. Lithium nitrate	Eysseltová and Orlova (2010)
Metal carbonates. Part 1. Solubility and related thermodynamic quantities of cadmium(II) carbonate in aqueous systems	Gamsjäger et al. (2011)
Potassium sulfate in water	Eysseltová and Bouaziz (2012)

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Rare earth metal iodides and bromides in water and aqueous systems. Part 1. Iodides	Mioduski *et al*. (2012)
Rare earth metal iodides and bromides in water and aqueous systems. Part 2. Bromides	Mioduski *et al*. (2013)
Alkaline earth carbonates in aqueous systems. Part 1. Introduction, Be and Mg	De Visscher *et al*. (2012)
Alkaline earth carbonates in aqueous systems. Part 2. Ca	De Visscher and Vanderdeelen (2012)
Rare earth metal fluorides in water and aqueous systems. Part 1. Scandium group (Sc, Y, La)	Mioduski *et al*. (2014)
Rare earth metal fluorides in water and aqueous systems. Part 2. Light lanthanides (Ce Eu)	Mioduski *et al*. (2014)
Rare earth metal fluorides in water and aqueous systems. Part 3. Heavy lanthanides (Gd Lu)	Mioduski *et al*. (2015)
Alkali metal nitrates. Part 2. Sodium nitrate	Eysseltová *et al*. (2017)
Lithium sulfate and its double salts in aqueous solutions	Sohr et al. (2017)

Table 3.

NEA published volumes

System	Reference
Uranium	Grenthe *et al.* (1992)
Americium	Silva *et al.* (1995)
Technetium	Rard *et al.* (1999)
Neptunium and plutonium	Lemire *et al.* (2001)
Update of uranium, neptunium, plutonium, americium and technetium	Guillaumont *et al.* (2003)
Nickel	Gamsjäger *et al.* (2005)
Selenium	Olin *et al.* (2005)
Zirconium	Brown *et al.* (2005)
Compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni and Zr with selected organic ligands	Hummel *et al.* (2005)
Solid solutions state-of-the-art report	Bruno *et al.* (2007)
Thorium	Rand *et al.* (2009)
Tin	Gamsjäger *et al.* (2012)
Iron Part 1	Lemire *et al.* (2013)