AGENCE DE L'OCDE POUR L'ÉNERGIE NUCLÉAIRE
OECD NUCLEAR ENERGY AGENCY

TDB-1

GUIDELINES FOR THE REVIEW PROCEDURE AND DATA SELECTION

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Guidelines for the Review Procedure and Data Selection

These guidelines provide the members of the various NEA specialist teams with information on the level of detail expected in the NEA review of chemical thermodynamics. It is important that the scope and the level of detail be consistent among the different reviews. The problems the experts have to cope with during the review are often similar, regardless of the characteristics of the key element.

These guidelines are based, to a large extent, on the experience with past reviews of chemical thermodynamics, and are complemented by documents addressing, in detail, various problem areas:

TDB-2 Guidelines on the extrapolation to zero ionic strength [99NEA]

TDB-3 Guidelines on the assignment of uncertainties [99NEA]

TDB-4 Guidelines for temperature corrections [99NEA]

TDB-5 Standards and conventions in TDB publications [99NEA]

TDB-6 Guidelines for the independent peer review of TDB reports [99NEA]

The following sections outline the procedure of selecting a value for a thermodynamic parameter (G_{m}, H_{m}, S_{m} or $C_{p,\mathrm{m}}$ of a species or of a reaction) based on experimental data. They include:

- No primary data source available
- One primary data source available
- Two or more primary data sources available.

1 No primary data source available

The principal aim of the TDB Project is to provide the user with a set of thermodynamic data that is complete, to the best of our knowledge, for the prediction of the chemical behaviour of a target element along its migration path from a deep repository to the biosphere. The composition of the aqueous phase can change drastically along the migration path, depending on the composition of the geological medium and on the influence of repository components. Various solid materials may determine the composition of the aqueous phase: concrete, bentonite (backfill materials), granite, basalt, salt, tuff, clays, anhydrite, and sediments, including surface materials. A review should therefore seek to include selected

data for all the species that can possibly contribute to the behaviour of the key element under these many conditions. This condition is possibly subject to constraints imposed by limited resources. Such constraints should be clearly stated in the introduction to the final report.

There are some standard restrictions that usually apply; these are discussed in the TDB-0 Guideline [99NEA].

It should also be noted, that it is an important feature of the TDB project that *only* original experimental data are evaluated, not estimates, values from compilations or secondary citations.

2 One primary data source available

Step 1: How did previous critical reviews judge this source? If it was judged negatively, what were the reasons?

Step 2: Are the experimental details given in the paper sufficient to judge the quality of the experiment? If so, is the experimental procedure satisfactory? If not, discard this source and proceed as described in Section 1.

Step 3: Have all possible side-reactions been considered in the evaluation of the experiment? If not, are any experimental data available that allow a re-evaluation? If the quantitative effects of the side-reactions cannot be estimated, one has to proceed as described in Section 1.

Step 4: Have all the necessary corrections been made by the author? (Examples are the junction potential in potentiometric measurements and possible complex formation of the metal ion with the anion of the inert salt.) If not, are sufficient details given in the paper that allow for these artifacts to be corrected? If not, this source probably has to be discarded unless the corrections can be estimated based on other, similar experiments of that kind.

Step 5: Does the datum refer to standard conditions (*cf.* Ref. [99NEA])? If not, the appropriate corrections have to be made:

a) Temperature corrections: use the temperature correction methods described in the TDB-4 Guideline [99NEA]. In many cases, however, especially in the case of equilibria involving aqueous species where the net change in the ionic charges is small, the influence of small temperature

changes on the equilibrium constant is smaller than its uncertainty. A correction from, *e.g.*, 18, 20 or 30°C to the 25°C reference temperature may be ignored in such cases. However, an increase of the uncertainty in the equilibrium constant could be appropriate within reasonable limits.

b) Pressure corrections: For large pressure corrections, no guidelines have been worked out. In this case, the problem should be addressed to NEA. For corrections from 1 atm (1.01325×10^5 Pa) to 1 bar (1.00000×10^5 Pa), a special conversion program has been developed and tested at the NEA Data Bank. Publications can thus be sent to the NEA for the conversion from old to new standard pressure. A detailed description of this conversion is given in the TDB-5 Guideline [99NEA].

c) Ionic strength corrections: See the corresponding guidelines, TDB-2 [99NEA]. An initial uncertainty, representing the 95% confidence interval, has to be assigned to each credible value. Outliers, if they are credible, should be treated as described in detail in the Guidelines for the Assignment of Uncertainties, TDB-3 [99NEA]. Analogies for any missing ion interaction coefficients will have to be made. The NEA should be consulted if there are any further problems. An additional result from the linear regression is the slope of the straight line, including its uncertainty. This slope represents $\Delta\varepsilon$, that is the stoichiometric sum of the ion interaction coefficients. Usually, the ion interaction coefficient of the target species with the oppositely charged inert salt component can be extracted. This value should be mentioned in the main text and listed in the table of ion interaction coefficients in an appendix of the review report.

Step 6: If the necessary corrections (if required) can be done, the data from this source can be selected. If the thermodynamic model used by the authors differs significantly from the one accepted by the TDB review or the original fitting is incorrect for other reasons, and if sufficient experimental data are given, in tables or figures, they should always be used to extract, by means of regression fits or other suitable methods, the thermodynamic data sought. If no or insufficient experimental data are given, the author(s) should be contacted, if possible, to see if the required data can be obtained.

If no experimental data are available, the thermodynamic data are selected as given in the source. An uncertainty must now be assigned to the data or datum extracted or given in the source. If experimental data are available, it is normally possible to estimate an uncertainty from the evaluation procedure (see also TDB-3 [99NEA]). If not, the assignment of an uncertainty is a difficult task because no statistical method can be used, and nevertheless the uncertainty should, as for all the selected data, represent the (statistically defined) 95 % confidence level. For this task, it is important that the reviewer has some experience with the method used in this experiment and knows its reliability, as well as the range of precision of the instruments. The assessment of such an uncertainty is thus highly subjective and may be called an "educated guess". If there are serious problems with this task, an experienced scientist who is familiar with that particular experimental method should be consulted.

Step 7: Describe and discuss the information gathered in Steps 1 through 5. If the discussion goes into considerable detail, this text will appear in an appendix ("Discussion of selected references", *cf.* [92GRE/FUG] of the review report. In any case, the level of detail should be sufficient for the reader (who can be assumed to have a background in thermodynamics) to understand the reasons why this primary data source has been accepted or rejected, respectively. The text in the main section should only contain a brief summary of this discussion and give the value if it has been accepted.

The main reason for creating a separate appendix containing discussion of individual publications is not to overload the main text with extensive technical details.

3 Two or more primary data sources available

In this case, it is necessary to go through Steps 1 to 5 and Step 7, as described in Section 2, for each single reference. Several outcomes are possible, as described below:

Case 1: All the primary data sources have to be discarded. In this case, proceed as described in Section 1.

Case 2: Only one credible data source remains. In this case, move to Step 6 of Section 2.

Case 3: Two or more credible data sources exist. An uncertainty, representing the 95% confidence interval, must be assigned to each datum, and a weighted average value calculated according to the method described in the Guidelines for the Assignment of Uncertainties, TDB-3 [99NEA].

References

[92GRE/FUG] Grenhe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H., *Chemical Thermodynamics of Uranium*, vol. 1 of *Chemical Thermodynamics*, Amsterdam: Elsevier Science Publishers B. V., 1992, 715 p. Cited pages 4

[99NEA] "TDB-0–TDB-6, TDB project guidelines", NEA Web site PDF documents, 1999, URL http://www.nea.fr/html/dbtdb/guidelines/guidelines.html. Cited pages 1, 1, 1, 1, 1, 2, 2, 2, 3, 3, 3, 4, 5