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


# TDB-3

# GUIDELINES FOR THE ASSIGNMENT OF UNCERTAINTIES

Hans Wanner
Minor additions by Erik Östhols

Version of 1st June 1999

Le Seine-St. Germain
12, Bd. des Îles
F-92130 Issy-les-Moulineaux
FRANCE

# Guidelines for the Assignment of Uncertainties

One of the objectives of the NEA Thermochemical Data Base (TDB) project is to provide an idea of the uncertainties associated with the data selected in this review. As a rule, the uncertainties define the range within which the corresponding data can be reproduced with a probability of 95% at any place and by any appropriate method. In many cases, statistical treatment is limited or impossible due to the availability of only one or few data points. A particular problem has to be solved when significant discrepancies occur between different source data. These guidelines outline the statistical procedures to be used for fundamentally different problems and explains the philosophy to be used when statistics are inapplicable. These rules should be followed consistently throughout the series of reviews within the TDB Project. Four fundamentally different cases are considered:

1. One source datum available
2. Two or more independent source data available
3. Several data available at different ionic strengths
4. Data at non-standard conditions: Procedures for data correction and recalculation.

## 1 One source datum

The assignment of an uncertainty to a selected value that is based on only one experimental source is a highly subjective procedure. In some cases, the number of data points the selected value is based on allows the use of the "root mean square" [82TAY] deviation of the data points $X_i$ to describe the standard deviation $s_X$ associated with the average $\overline{X}$:

$$s_X = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \overline{X})^2} \qquad (1)$$

The standard deviation $s_X$ is thus calculated from the dispersion of the equally weighted data points $X_i$ around the average $\overline{X}$, and the probability is 95% that an $X_i$ is within $\overline{X} \pm 1.96\, s_X$), see Taylor [82TAY, *pp*.244-245]. The standard deviation $s_X$ is a measure of the precision of the experiment and does not include any systematic errors.

Many authors report standard deviations $s_X$ calculated with Eq. (1) (but often not multiplied by 1.96), but these do not represent the quality of the reported

values in absolute terms. It is thus important not to confuse the standard deviation $s$ with the uncertainty $\sigma$. The latter reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors $s_j$ that may be involved. The uncertainty $\sigma$ can be calculated with Eq. (2), assuming that the systematic errors are independent.

$$\sigma_{\overline{X}} = \sqrt{s_X^2 + \sum_j (s_j^2)} \tag{2}$$

The estimation of the systematic errors $s_j$ (which, of course, have to relate to $\overline{X}$ and be expressed in the same unit) can only be made by a person who is familiar with the experimental method. If the reviewer feels he does not have enough experience with the experimental method to estimate the systematic errors, an experienced scientist should be consulted. The uncertainty $\sigma$ should correspond to the 95% confidence level preferred in this review. It should be noted that for all the corrections and recalculations that need to be made (*e.g.*, temperature or ionic strength corrections) the rules of the propagation of errors must be followed, as outlined in Section 4.

More often, the determination of $s_X$ is not possible because either only one or two data points are available, or the authors did not report the individual values. The uncertainty $\sigma$ in the resulting value can still be estimated using Eq. (2) assuming that $s_X^2$ is much smaller than $\sum_j (s_j^2)$, which is usually the case anyway.

## 2 Two or more independent source data

Frequently, two or more experimental data sources are available, reporting experimental determinations of the desired thermodynamic data. In general, the quality of these determinations varies widely, and the data have to be weighted accordingly for the calculation of the mean. Instead of assigning weight factors, the individual source data $X_i$ are provided with an uncertainty $\sigma_i$ that also includes all systematic errors and represents the 95% confidence level, as described in Section 1. The weighted mean $\overline{X}$ and its uncertainty $\sigma_{\overline{X}}$ are then calculated according to Eqs. (3) and (4).

$$\overline{X} \equiv \frac{\sum_{i=1}^{N} \left( \frac{X_i}{\sigma_i^2} \right)}{\sum_{i=1}^{N} \left( \frac{1}{\sigma_i^2} \right)} \tag{3}$$

$$\sigma_{\overline{X}} = \sqrt{\frac{1}{\sum_{i=1}^{N} \left( \frac{1}{\sigma_i^2} \right)}} \tag{4}$$

Eqs. (3) and (4) may only be used if all the $X_i$ belong to the same parent distribution. If there are serious discrepancies among the $X_i$, one should proceed as described below under "Discrepancies". It can be seen from Eq. (4) that $\sigma_{\overline{X}}$ is directly dependent on the absolute magnitude of the $\sigma_i$ values, and not on the dispersion of the data points around the mean. This is reasonable because there are no discrepancies among the $X_i$, and because the $\sigma_i$ values already represent the 95% confidence level. The selected uncertainty $\sigma_{\overline{X}}$ will therefore also represent the 95% confidence level.

In cases where all the uncertainties are equal $\sigma_i = \sigma$, Eqs. (3) and (4) reduce to Eqs. (5) and (6).

$$\overline{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{5}$$

$$\sigma_{\overline{X}} = \frac{\sigma}{\sqrt{N}} \tag{6}$$

**Example 1:**

Five data sources report values for the thermodynamic quantity $X$. The reviewer has assigned uncertainties that represent the 95% confidence level as described in Section 1.

| $i$ | $X_i$ | $\sigma_i$ |
|---|---|---|
| 1 | 25.3 | 0.5 |
| 2 | 26.1 | 0.4 |
| 3 | 26.0 | 0.5 |
| 4 | 24.85 | 0.25 |
| 5 | 25.0 | 0.6 |

According to Eqs. (3) and (4), the following result is obtained:

$$\overline{X} = 25.3 \pm 0.2$$

The calculated uncertainty $\sigma_{\overline{X}} = 0.2$ appears relatively small but is statistically correct, for the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (4), $\sigma_{\overline{X}}$ will always come out smaller than the smallest $\sigma_i$. Assuming $\sigma_4 = 0.10$ instead of 0.25 would yield $\overline{X} = (25.0 \pm 0.1)$, and $\sigma_4 = 0.60$ would result in $\overline{X} = (25.6 \pm 0.2)$. In fact, the values $(X_i \pm \sigma_i)$ in this example are at the limit of consistency, that is, the range $(X_4 \pm \sigma_4)$ does not overlap with the ranges $(X_2 \pm \sigma_2)$ and $(X_3 \pm \sigma_3)$. There might be a better way to solve this problem. Three possible alternatives seem more reasonable:

i. The uncertainties $\sigma_i$ are reassigned because they appear too optimistic after further consideration. Some assessments may have to be reconsidered and the uncertainties reassigned. For example, multiplying all the $\sigma_i$ by 2 would yield $\overline{X} = (25.3 \pm 0.3)$.

ii. If reconsideration of the previous assessments gives no evidence for reassigning the $X_i$ and $\sigma_i$ (95% confidence level) values listed above, the statistical conclusion will be that all the $X_i$ do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical explanation). The values for $i = 1$, 4 and 5 might be considered as belonging to Group A and the values for $i = 2$ and 3 to Group B. The weighted average of the values in Group A is $X_A(i = 1, 4, 5) = (24.95 \pm 0.21)$ and of those in Group B $X_B(i = 2, 3) = (26.06 \pm 0.31)$, the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under "Discrepancies" (Case I). $X_A$ and $X_B$ are averaged (straight average, there is no reason for giving $X_A$ a larger weight than $X_B$), and $\sigma_{\overline{X}}$ is chosen in such a way that it covers the complete ranges of expectancy of $X_A$ and $X_B$. The selected value is then $\overline{X} = (25.5 \pm 0.9)$.

iii. Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then $\overline{X} = (25.45 \pm 1.05)$, which is rounded according to the rules in Section 4 to $\overline{X} = (25.4 \pm 1.1)$.

## Discrepancies

Two data are called discrepant if they differ significantly, *i.e.*, their uncertainty ranges do not overlap. In this context, two cases of discrepancies are considered. Case I: Two significantly different source data are available. Case II: Several, mostly consistent source data are available, one of them being significantly different, *i.e.*, an "outlier".

**Case I:** This is a particularly difficult case because the number of data points is obviously insufficient to allow the preference of one of the two values. If there is absolutely no way of discarding one of the two values and selecting the other, the only solution is to average the two source data in order to obtain the selected value, because the underlying reason for the discrepancy must be unrecognized systematic errors. There is no point in calculating a weighted average, even if the

two source data have been given different uncertainties, because there is obviously too little information to give even only limited preference to one of the values. The uncertainty $\sigma_{\overline{X}}$ assigned to the selected mean $\overline{X}$ has to cover the range of expectation of both source data $X_1$, $X_2$, as shown in Eq. (7).

$$\sigma_{\overline{X}} \;=\; \left|X_i - \overline{X}\right| + \sigma_{\max} \tag{7}$$

where $i = 1, 2$, and $\sigma_{\max}$ is the larger of the two uncertainties $\sigma_i$, see Example 1.ii and Example 2.

**Example 2:**

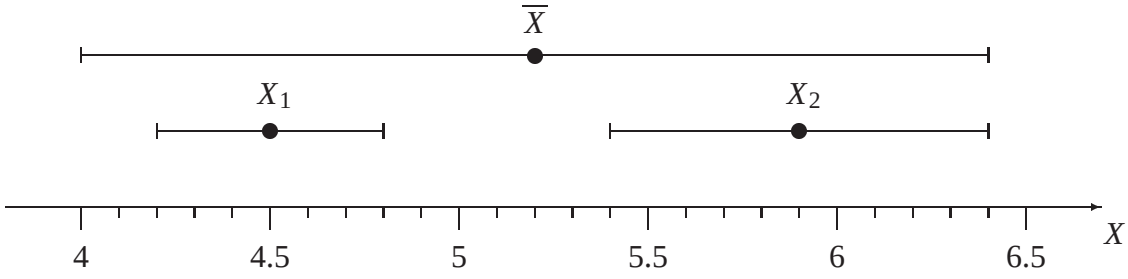
The following credible source data are given:

$$\begin{aligned} X_1 &= 4.5 \pm 0.3 \\ X_2 &= 5.9 \pm 0.5 \end{aligned}$$

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory, and there is no justification to discard one of the data. The selected value is then:

$$\overline{X} \;=\; 5.2 \pm 1.2$$

Illustration for Example 2:




**Case II:** This problem can often be solved by either discarding the outlying data point, or by providing it with a large uncertainty to lower its weight. If, however, the outlying value is considered to be of high quality and there is no reason to discard all the other data, this case is treated in a way similar to Case I. Example 3 illustrates the procedure.

**Example 3:**

The following data points are available. The reviewer has assigned the uncertainties and sees no justification for any change.

| i | $X_i$ | $\sigma_i$ |
|---|---|---|
| 1 | 4.45 | 0.35 |
| 2 | 5.9 | 0.5 |
| 3 | 5.7 | 0.4 |
| 4 | 6.0 | 0.6 |
| 5 | 5.2 | 0.4 |

There are two sets of data that, statistically, belong to different parent distributions A and B. According to Eqs. (3) and (4), the following average values are found for the two groups: $X_A(i = 1) = (4.45 \pm 0.35)$ and $X_B(i = 2, 3, 4, 5) = (5.62 \pm 0.23)$. The selected value will be the straight average of $X_A$ and $X_B$, analogous to Example 1:

$$\overline{X} = 5.0 \pm 0.9.$$

# 3 Several data at different ionic strengths

The extrapolation procedure used in this review is the SIT method outlined in the NEA Guidelines for the Extrapolation to Zero Ionic Strength (TDB-2) [98GRE/WAN]. The objective of the TDB project is to provide selected data sets at infinite dilution for aqueous species. Equilibrium constants determined at different ionic strengths can, according to the SIT method, be extrapolated to $I = 0$ with a linear regression model, yielding as the intercept the desired equilibrium constant at $I = 0$, and as the slope the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficient of the target species can usually be extracted from $\Delta\varepsilon$, and it will be published in the review report as a selected value, because the user of these data needs this information to extrapolate back from $I = 0$.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to $I = 0$ should be carried out according to the procedure described in Section 4.

If sufficient data are available at different ionic strengths and in the same inert salt medium, a weighted linear regression will be the appropriate way to obtain both the constant at $I = 0$, $\overline{X}^\circ$, and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar ($\text{mol} \cdot \text{dm}^{-3}$, M) to the molal ($\text{mol} \cdot \text{kg}^{-1}$, m) scale, as described in TDB-5 (Standards and conventions for TDB publications). The second step is the assignment of an uncertainty $\sigma_i$, representing the 95% confidence level, to each data point $X_i$ at the molality $m_{k,i}$, according to the rules described in Section 1. A large number of commercial and public domain computer programs and routines exist for weighted linear regressions. The

subroutine published by Bevington [69BEV, *pp.*104-105], has been used for the calculations in the examples of these guidelines. Eqs. (8) through (12) present the equations that are used for the calculation of the intercept $\overline{X}^\circ$ and the slope $\Delta\varepsilon$:

$$\overline{X}^\circ = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2}\right) \tag{8}$$

$$-\Delta\varepsilon = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2}\right) \tag{9}$$

$$\sigma_{\overline{X}^\circ} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}} \tag{10}$$

$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}} \tag{11}$$

$$\text{where} \qquad \Delta = \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\right)^2 \tag{12}$$

In this way, the uncertainties $\sigma_i$ are not only used for the weighting of the data in Eqs. (8) and (9), but also for the calculation of the uncertainties $\sigma_{\overline{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ in Eqs. (10) and (11). If the $\sigma_i$ represent the 95% confidence level, $\sigma_{\overline{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line but rather directly on their absolute uncertainties $\sigma_i$.

**Example 4:**

Ten independent determinations of $\log_{10}^{*}\beta$ for the reaction

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^+ + H^+$$

are available in $HClO_4/NaClO_4$ media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression, $(\log_{10}^{*}\beta + 2D)$ *vs.* $m_k$, according to the formula $\log_{10}^{*}\beta + 2D = \log_{10}^{*}\beta^\circ - \Delta\varepsilon\, m_k$, will yield the correct values for the intercept $\log_{10}^{*}\beta^\circ$ and the slope $\Delta\varepsilon$. In this case, $m_k$ corresponds to the molality of $ClO_4^-$.

| i | $m_{ClO_4^-,i}$ | $\log_{10}{}^{*}\beta_i + 2D$ | $\sigma_i$ |
|---|---|---|---|
| 1 | 0.05 | 1.88 | 0.10 |
| 2 | 0.25 | 1.86 | 0.10 |
| 3 | 0.51 | 1.73 | 0.10 |
| 4 | 1.05 | 1.84 | 0.10 |
| 5 | 2.21 | 1.88 | 0.10 |
| 6 | 0.52 | 1.89 | 0.11 |
| 7 | 1.09 | 1.93 | 0.11 |
| 8 | 2.32 | 1.78 | 0.11 |
| 9 | 2.21 | 2.03 | 0.10 |
| 10 | 4.95 | 2.00 | 0.32 |

Note: $D$ is the Debye-Hückel term, see NEA Guidelines on Extrapolation to Zero Ionic Strength (TDB-2) [98GRE/WAN].

The results of the linear regression are:

$$\begin{aligned} \text{intercept} &= 1.837 \pm 0.054 = \log_{10}{}^{*}\beta^\circ \\ \text{slope} &= 0.029 \pm 0.036 = -\Delta\varepsilon \end{aligned}$$

Calculation of the ion interaction coefficient $\varepsilon_{(UO_2F^+,ClO_4^-)} = \Delta\varepsilon + \varepsilon_{(UO_2^{2+},ClO_4^-)} - \varepsilon_{(H^+,ClO_4^-)}$: From $\varepsilon_{(UO_2^{2+},ClO_4^-)} = (0.46 \pm 0.03)$, $\varepsilon_{(H^+,ClO_4^-)} = (0.14 \pm 0.02)$ (see NEA Guidelines on Extrapolation to Zero Ionic Strength, TDB-2) [98GRE/WAN] and the slope of the linear regression, $\Delta\varepsilon$ =$(-0.03 \pm 0.04)$, it follows that $\varepsilon_{(UO_2F^+,ClO_4^-)} = (0.29 \pm 0.05)$. Note that the uncertainty ($\pm 0.05$) is obtained based on the rules of error propagation as described in Section 4:

$$\sigma = \sqrt{(0.04)^2 + (0.03)^2 + (0.02)^2}$$

The resulting selected values are thus

$$\begin{aligned} \log_{10}{}^{*}\beta^\circ &= 1.84 \pm 0.05 \\ \varepsilon_{(UO_2F^+,ClO_4^-)} &= 0.29 \pm 0.05. \end{aligned}$$

## Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section 2. Again, two cases can be defined. Case I: Only two data are available. Case II: An "outlier" cannot be discarded. If only one data point is available, the procedure for correction to zero ionic strength outlined in Section 4 should be followed.

**Case I:** If only two source data are available, there will be no straightforward way to decide whether or not these two data points belong to the same parent

distribution unless either the slope of the straight line is known or the two data refer to the same ionic strength. Drawing a straight line right through the two data points is an inappropriate procedure because all the errors associated with the two source data would accumulate and may lead to highly erroneous values of $\log_{10} K^\circ$ and $\Delta\varepsilon$. In this case, an ion interaction coefficient for the key species in the reaction in question may be selected by anology (charge is the most important parameter), and a straight line with the slope $\Delta\varepsilon$ as calculated may then be drawn through each data point. If there is no reason to discard one of the two data points based on the quality of the underlying experiment, the selected value will be the unweighted average of the two standard state data obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section 2. It should be mentioned that the ranges of expectancy of the corrected values at $I = 0$ are given by their uncertainties which are based on the uncertainties of the source data at $I \neq 0$ and the uncertainty in the slope of the straight line. The latter uncertainty is not an estimate but is calculated from the uncertainties in the ion interaction coefficients involved, according to the rules of error propagation outlined in Section 4. The ion interaction coefficients estimated by analogy will be listed in the table of selected ion interaction coefficients, but they will be flagged as estimates.

**Case II. Outliers and inconsistent data sets:** This case includes situations where it is difficult to decide whether or not a large number of points belong to the same parent distribution. There is no general rule on how to solve this problem, and decisions are left to the judgement of the reviewer. For example, if eight data points follow a straight line reasonably well and two lie way out, it may be justified to discard the "outliers". If, however, the eight points are scattered considerably and two points are just a bit further out, one can probably not consider them as "outliers". It depends on the particular case and on the judgement of the reviewer whether it is reasonable to increase the uncertainties of the data to reach consistency, or whether the slope $\Delta\varepsilon$ of the straight line should be estimated by analogy.

**Example 5:**

Six reliable determinations of the equilibrium constant $\log_{10} \beta$ of the reaction

$$UO_2^{2+} + SCN^- \rightleftharpoons UO_2SCN^+ \tag{13}$$

are available in different electrolyte media:

$I_c$ = 0.1 M ($KNO_3$): $\log_{10}\beta(13) = 1.19 \pm 0.03$
$I_c$ = 0.33 M ($KNO_3$): $\log_{10}\beta(13) = 0.90 \pm 0.10$
$I_c$ = 1.0 M ($NaClO_4$): $\log_{10}\beta(13) = 0.75 \pm 0.03$
$I_c$ = 1.0 M ($NaClO_4$): $\log_{10}\beta(13) = 0.76 \pm 0.03$
$I_c$ = 1.0 M ($NaClO_4$): $\log_{10}\beta(13) = 0.93 \pm 0.03$
$I_c$ = 2.5 M ($NaNO_3$): $\log_{10}\beta(13) = 0.72 \pm 0.03$

The uncertainties are assumed to represent the 95% confidence level. From the values at $I_c = 1$ M, it can be seen that there is a lack of consistency in the data, and that a linear regression like in Example 4 would not be appropriate. Instead, the use of $\Delta\varepsilon$ values from reactions of the same charge type is encouraged. Analogies with $\Delta\varepsilon$ are more reliable than analogies with single $\varepsilon$ values due to cancelling effects. For the same reason, the dependency of $\Delta\varepsilon$ on the type of electrolyte is often smaller than for single $\varepsilon$ values.

A reaction of the same charge type as Reaction 13, and for which $\Delta\varepsilon$ is well known, is

$$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+ \qquad (14)$$

The value of $\Delta\varepsilon(14) = -(0.25 \pm 0.02)$ was obtained from a linear regression using 16 experimental data between $I_c = 0.1$ M and $I_c = 3$ M Na(Cl,$ClO_4$) [92GRE/FUG]. It is thus assumed that

$$\Delta\varepsilon(13) = \Delta\varepsilon(14) = -0.25 \pm 0.02$$

The correction of $\log_{10}\beta(13)$ to $I_c = 0$ is done using the SIT equation, *cf.* TDB-2 [98GRE/WAN], which uses molal units:

$$\log_{10}\beta + 4D = \log_{10}\beta^\circ - \Delta\varepsilon I_m \qquad (15)$$

$D$ is the Debye-Hückel term in molal units and $I_m$ the ionic strenght converted to molal units by using the conversion factors listed in [76BAE/MES, *p.* 439]. The following list gives the details of this calculation. The resulting uncertainties in $\log_{10}\beta$ are obtained based on the rules of error propagation as described in Section 4.

| $I_m$ | electrolyte | $\log_{10}\beta$ | $4D$ | $\Delta\varepsilon I_m$ | $\log_{10}\beta^\circ$ |
|---|---|---|---|---|---|
| 0.101 | $KNO_3$ | $1.19 \pm 0.03$ | 0.438 | -0.025 | 1.68±0.03[(a)] |
| 0.335 | $KNO_3$ | $0.90 \pm 0.10$ | 0.617 | -0.084 | 1.65±0.10[(a)] |
| 1.050 | $NaClO_4$ | $0.75 \pm 0.03$ | 0.822 | −0.263 | 1.31±0.04 |
| 1.050 | $NaClO_4$ | $0.76 \pm 0.03$ | 0.822 | −0.263 | 1.32±0.04 |
| 1.050 | $NaClO_4$ | $0.93 \pm 0.03$ | 0.822 | −0.263 | 1.49±0.04 |
| 2.714 | $NaNO_3$ | $0.72 \pm 0.03$ | 0.968 | −0.679 | 1.82±0.13[(a)] |

[(a)] These values were corrected for the formation of the nitrate complex $UO_2NO_3^+$ by using $\log_{10} K(UO_2NO_3^+) = (0.30 \pm 0.15)$ [92GRE/FUG].

As was expected, the resulting values $\log_{10}\beta^\circ$ are inconsistent and have therefore to be treated as described in Case I of Section 2. That is, the selected value will be the unweighted average of $\log_{10}\beta^\circ$, and its uncertainty will cover the entire range of expectancy of the six values. A weighted average would only be justified if the six values of $\log_{10}\beta^\circ$ were consistent. The result is

$$\log_{10}\beta^\circ = 1.56 \pm 0.39$$

# 4 Procedures for data handling

This section presents rules and guidelines for the following topics:

- Correction to zero ionic strength
- Propagation of errors
- Rounding
- Significant digits

## Correction to zero ionic strength

The correction of experimental data to zero ionic strength is necessary in all cases where a linear regression is impossible or appears inappropriate. The method used throughout the review is the specific ion interaction method (SIT). This method is described in detail in the NEA Guidelines on Extrapolation to Zero Ionic Strength (TDB-2) [98GRE/WAN]. Two variables are needed for this correction, and both have to be provided with an uncertainty at the 95% confidence level: the experimental source value, $\log_{10} K$ or $\log_{10}\beta$, and the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficients (see tables in the NEA

Guidelines on Extrapolation to Zero Ionic Strength, TDB-2 [98GRE/WAN]) required to calculate $\Delta\varepsilon$ may not all be known. Missing values therefore need to be estimated. It is recalled that the electric charge has the most significant influence on the magnitude of the ion interaction coefficients, and that it is in general more reliable to estimate $\Delta\varepsilon$ from known reactions of the same charge type, rather than to estimate single $\varepsilon$ values. The uncertainty of the corrected value at $I = 0$ is calculated by taking into account the propagation of errors, as described below. It is recalled that the ionic strength is frequently given in moles per $dm^3$ of solution (molar, M) and has to be converted to moles per kg $H_2O$ (molal, m), as the SIT equation requires. A table of conversion factors for the most common inert salts given by Baes and Mesmer [76BAE/MES, *p.* 439] is represented in TDB-5 (Standards and conventions for TDB publications) [98WAN/ÖST].

**Example 6:**

For the equilibrium constant of the reaction

$$M^{3+} + 2H_2O(l) \rightleftharpoons M(OH)_2^+ + 2H^+ \qquad (16)$$

only one credible determination in 3 M $NaClO_4$ solution is known, $\log_{10}{}^{*}\beta(16) = -6.31$, to which an uncertainty of $\pm 0.12$ has been assigned. The ion interaction coefficients are as follows:

$$\begin{aligned} \varepsilon_{(M^{3+},ClO_4^-)} &= 0.56 \pm 0.07 \\ \varepsilon_{(M(OH)_2^+,ClO_4^-)} &= 0.26 \pm 0.11 \\ \varepsilon_{(H^+,ClO_4^-)} &= 0.14 \pm 0.01 \end{aligned}$$

$\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily:

$$\begin{aligned} \Delta\varepsilon &= \varepsilon_{(M(OH)_2^+,ClO_4^-)} + 2\varepsilon_{(H^+,ClO_4^-)} - \varepsilon_{(M^{3+},ClO_4^-)} = -0.02 \\ \sigma_{\Delta\varepsilon} &= \sqrt{(0.11)^2+(2\times 0.01)^2+(0.07)^2} = 0.13 \end{aligned}$$

The two variables are thus:

$$\begin{aligned} \log_{10}{}^{*}\beta(16) &= -6.31 \pm 0.12 \\ \sigma_{\Delta\varepsilon} &= -0.02 \pm 0.13 \end{aligned}$$

According to the SIT method, the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}{}^{*}\beta + 6D = \log_{10}{}^{*}\beta^{\circ} - \Delta\varepsilon\, m_{ClO_4^-}$$

$D$ is the Debye-Hückel term: $D = 0.509\sqrt{I_m}/(1 + 1.5\sqrt{I_m})$. The ionic strength $I_m$ and the molality $m_{ClO_4^-}$ ($I_m \approx m_{ClO_4^-}$) have to be expressed in molal units, 3 M $NaClO_4$ corresponding to 3.5 m $NaClO_4$ [76BAE/MES], giving $D = 0.25$. This results in

$$\log_{10}{}^{*}\beta^{\circ}(16) = -4.88.$$

The uncertainty in $\log_{10}{}^{*}\beta^{\circ}(16)$ is calculated from the uncertainties in $\log_{10}{}^{*}\beta(16)$ and $\Delta\varepsilon$:

$$\sigma_{\log_{10}{}^{*}\beta^{\circ}} = \sqrt{\sigma^2_{\log_{10}{}^{*}\beta} + \left(m_{ClO_4^-}\,\sigma^2_{\Delta\varepsilon}\right)^2} = \sqrt{(0.12)^2 + (3.5 \times 0.12)^2} = 0.44$$

The selected value is:

$$\log_{10}{}^{*}\beta^{\circ}(16) \quad = \quad -4.9 \pm 0.4.$$

## Propagation of errors

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties, the propagation of these uncertainties has to be taken into account in a correct way. A detailed outline of the propagation of errors is given by Bevington [69BEV]. A simplified form of the general formula for error propagation is given by Eq. (17), supposing that $X$ is a function of $Y_1, Y_2, \ldots, Y_N$.

$$\sigma_X^2 \quad = \quad \sum_{i=1}^{N} \left(\frac{\partial X}{\partial Y_i}\sigma_{Y_i}\right)^2 \tag{17}$$

Eq. (17) can be used only if the variables $Y_1, Y_2, \ldots, Y_N$ are independent or if their uncertainties are small, that is the covariances can be disregarded. One of these two assumptions can almost always be made in chemical thermodynamics, and Eq. (17) can thus almost universally be used in this review. Eqs. (18) through (22) present explicit formulae for a number of frequently encountered algebraic expressions, where $c$, $c_1$, $c_2$ are constants.

$$X = c_1Y_1 \pm c_2Y_2 : \qquad \sigma_X^2 \;=\; (c_1\sigma_{Y_1})^2 + (c_2\sigma_{Y_2})^2 \tag{18}$$

$$X = \pm cY_1Y_2 \;\text{ and }\; X = \pm\frac{cY_1}{Y_2} : \qquad \left(\frac{\sigma_X}{X}\right)^2 \;=\; \left(\frac{\sigma_{Y_1}}{Y_1}\right)^2 + \left(\frac{\sigma_{Y_2}}{Y_2}\right)^2 \tag{19}$$

$$X = c_1Y^{\pm c_2} : \qquad \frac{\sigma_X}{X} \;=\; c_2\frac{\sigma_Y}{Y} \tag{20}$$

$$X = c_1\,e^{\pm c_2Y} : \qquad \frac{\sigma_X}{X} \;=\; c_2\sigma_Y \tag{21}$$

$$X = c_1\ln(\pm c_2Y) : \qquad \sigma_X \;=\; c_1\frac{\sigma_Y}{Y} \tag{22}$$

Here are some examples to illustrate how to use these formulae. The values have not been rounded.

**Example 7:**

$$\begin{aligned}\text{Eq. (18)}: \quad \Delta_r G_m &= 2[-(277.4 \pm 4.9)]\,\text{kJ}\cdot\text{mol}^{-1} \\ &\quad - [-(467.3 \pm 6.2)]\,\text{kJ}\cdot\text{mol}^{-1} \\ \Delta_r G_m &= -(87.5 \pm 11.6)\,\text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

$$\text{Eq. (19)}: \quad K = \frac{(0.038\pm0.002)}{(0.0047\pm0.0005)} = (8.09 \pm 0.92)$$

$$\text{Eq. (20)}: \quad K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$$

$$\text{Eq. (21)}: \quad K^\circ = e^{\frac{-\Delta_r G^\circ_m}{RT}}; \qquad \begin{aligned}\Delta_r G^\circ_m &= -(2.7 \pm 0.3)\,\text{kJ}\cdot\text{mol}^{-1} \\ R &= 8.3145\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ T &= 298.15\,\text{K}\end{aligned}$$

$$K^\circ = 2.97 \pm 0.36$$

Note that powers of 10 have to be reduced to powers of $e$, *i.e.*, the variable has to be multiplied by ln(10), *e.g.*:

$$\log_{10} K = (2.45 \pm 0.10); \quad K = 10^{\log_{10} K} = e^{(\ln(10)\ \log_{10} K)} = (282 \pm 65)$$

$$\text{Eq. (22)}: \quad \Delta_r G^\circ_m = -RT \ln K^\circ; \qquad \begin{aligned}K^\circ &= (8.2 \pm 1.2) \times 10^6 \\ R &= 8.3145\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ T &= 298.15\,\text{K}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\circ_m &= -(39.46 \pm 0.36)\,\text{kJ}\cdot\text{mol}^{-1} \\ \ln K^\circ &= 15.92 \pm 0.15 \\ \log_{10} K^\circ &= \ln K^\circ / \ln(10) = 6.91 \pm 0.06\end{aligned}$$

Again, it can be seen that the uncertainty in $\log_{10} K^\circ$ cannot be the same as in $\ln K^\circ$. The constant conversion factor of $\ln(10) = 2.303$ is also to be applied to the uncertainty.

**Example 8:**

Solubility curves as a function of some variable, e. g. pH, are often used in the discussions in the TDB books. To plot uncertainty limits of such curves, it is often possible to use simple error propagation formulae. As an example, consider the solubility of some metal cation $Me^{n+}$ as a function of pH, where we have the following set of equilibria:

$$\begin{aligned} \mathrm{MeO}_{\frac{n}{2}}(s) + n\mathrm{H}^+ &\rightleftharpoons \mathrm{Me}^{n+} + \tfrac{n}{2}\mathrm{H_2O} & K_{s,0} \\ \mathrm{Me}^{n+} + \mathrm{H_2O} &\rightleftharpoons \mathrm{Me(OH)}^{n-1} + \mathrm{H}^+ & {}^*\beta \\ \mathrm{Me}^{n+} + 3\mathrm{H_2O} &\rightleftharpoons \mathrm{Me(OH)}_3^{n-3} + 3\mathrm{H}^+ & {}^*\beta_3 \end{aligned}$$

Then we can write the total solubility of $Me^{n+}$, which equals the total concentration S in solution of all Me-containing species as a function of $[H^+]$ as follows, ignoring the activity of water:

$$S = K_{s,0}[H^+]^n + K_{s,0}{}^*\beta_1[H^+]^{n-1} + K_{s,0}{}^*\beta_3[H^+]^{n-3} \tag{23}$$

We can then make use of Eqs. (18) and (19), considering the stability constants as independent stochastic variables, which gives the total uncertainty in the solubility:

$$\begin{aligned} \sigma_S^2 \;=\; & (\sigma_{K_{s,0}}[H^+]^n)^2 + ([H^+]^{n-1})^2\left((\sigma_{K_{s,0}{}^*\beta})^2 + (\sigma_{{}^*\beta}K_{s,0})^2\right) + \\ & ([H^+]^{n-3})^2\left((\sigma_{K_{s,0}{}^*\beta_3})^2 + (\sigma_{{}^*\beta_3}K_{s,0})^2\right) \end{aligned} \tag{24}$$

In this way, we obtain the total uncertainty of the solubility as a function of pH. The uncertainties in the constants are usually given as $\sigma_{\log_{10} X}$, so to use them in Eq. (24), we have to use Eq. (22):

$$\sigma_{K_{s,0}} = \ln(10) K_{s,0} \sigma_{\log_{10} K_{s,0}}$$

Eventually, we want to take logarithms of Eq. (24), since we usually plot $\log_{10} S$ rather than S itself. We again use Eq. (22):

$$\sigma_{\log_{10} S} = \frac{\sigma_S}{S \ln(10)}$$

## Rounding

The standard rules to be used for rounding are:

i. When the digit following the last digit to be retained is less than 5, the last digit retained is kept unchanged.

ii. When the digit following the last digit to be retained is greater than 5, the last digit retained is increased by 1.

iii. When the digit following the last digit to be retained is 5 and

   (a) there are no digits (or only zeroes) beyond the 5, an odd digit in the last place to be retained is increased by 1 while an even digit is kept unchanged.

(b) other non-zero digits follow, the last digit to be retained is increased by 1, whether odd or even.

This procedure avoids introducing a systematic error from always dropping or not dropping a 5 after the last digit retained.

When adding or subtracting, the result is rounded to the number of decimal places (not significant digits) in the term with the least number of places. In multiplication and division, the results are rounded to the number of significant digits in the term with the least number of significant digits.

In general, all operations should be carried out in full, and only the final results should be rounded, in order to avoid the loss of information from repeated rounding. For this reason, several additional digits are carried in all calculations until the final selected set of data is developed (see NEA Guidelines for data selection, TDB-1), and only then are data rounded.

## Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

Example: $3.478 \pm 0.008$
$3.48 \pm 0.01$
$2.8 \pm 0.4$

In the case of auxiliary data or values that are used for later calculations, it is often not convenient to round to the last significant digit. In the value $(4.85 \pm 0.26)$, for example, the "5" is close to being significant and should be carried along a recalculation path in order to avoid loss of information. In particular cases, where the rounding to significant digits could lead to slight internal inconsistencies, digits with no significant meaning in absolute terms are nevertheless retained. The uncertainty of a selected value always contains the same number of digits after the decimal point as the value itself.

In some cases, reaction data obtained directly from equilibrium measurements, have smaller uncertainties than the data of formation of the species involved in the reaction. Using the data of formation for calculating the reaction data then leads to unreasonably high uncertainties. A table of selected reaction data will therefore be published in each volume.

# References

[69BEV] Bevington, P. R., Data reduction and error analysis for the physical sciences, New York: McGraw-Hill, 1969, 336 pages. 69BEV, 2182 7, 13

[76BAE/MES] Baes, Jr., C. F., Mesmer, R. F., The hydrolysis of cations, New York: Wiley & Sons, 1976, 489 pages. . . 76BAE/MES, 683 10, 12, 13

[82TAY] Taylor, J. R., An introduction to error analysis: The study of uncertainties in physical measurements, Mill Valley, CA, U. S. A.: University Science Books, 1982, 270 pages. 82TAY, 2180 1, 1

[92GRE/FUG] Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A., Nguyen-Trung, C., Wanner, H., Chemical Thermodynamics of Uranium, Volume 1 of Chemical Thermodynamics, Amsterdam: Elsevier Science Publishers B. V., 1992, 715 pages. 92GRE/FUG, 1000 10, 11

[98GRE/WAN] Grenthe, I., Wanner, H., TDB-2: Guidelines for the extrapolation to zero ionic strength, Technical report, OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France, 1998, 35 pages. . . . . 98GRE/WAN, 6003 6, 8, 8, 10, 11, 12

[98WAN/ÖST] Wanner, H., Östhols, E., TDB-1: Guidelines for the review procedure and data selection, Technical report, OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France, 1998, 6 pages. . . . . 98WAN/OST3, 5673 12