

## General comments

When we got access to the draft of the NEA-TDB review on the thermodynamics of Np and Pu, of course, our first interest was directed towards the review of our extensive work in the field of the thermodynamics of Np(V). Therefore most of the comments worked out in the present manuscript concern the following publications: the RCM and KfK reports (in German) [91KIM/KLE, 94RUN/KIM] and [94NEC/KIM], respectively, the papers [94NEC/RUN, 95NEC/RUN, 95NEC/FAN, 95FAN/NEC, 96FAN/NEC, 97NEC/FAN], and two papers of our former coworkers G. Meinrath [94MEI] and W. Runde [96RUN/NEU].

We noticed very soon that the reviewer of this section (P. Vitorge) favors the studies from his own laboratory in an incredible way and disregards results from other authors, in particular those of our group. The reviewer takes each opportunity to discredit the papers from “Kim’s group”. Two of the most often cited pretended “shortcomings” in our papers are “problems with pH electrode calibration” and “inconsistencies” among our results. In order to achieve an objective judgement of our pH measurements, we would appreciate a second reviewer to read the paper [96FAN/NEC], which clearly shows that in all the papers mentioned above, correct measurements were made to determine the quantities of interest, i.e. the concentrations of  $H^+$ ,  $OH^-$  and  $CO_3^{2-}$ . Some of the arguments documented in this paper are also mentioned in the present manuscript. More detailed information could be available from our earlier report [Neck, Fanghänel, Kim, FZKA 5599 (1995)] or by personal communication.

The second argument (“inconsistencies” among our results) is exclusively based on untrue statements, on obscure calculations of the reviewer himself, leading to nonsensical data and conclusions, which were never published or stated in our papers. In some of the “reviews” important information from our papers is just omitted, not even mentioned. We have the strong impression that some of the reviewer’s mistakes or incorrect statements were not accidentally, but on purpose, with the intention to discredit our work. Possibly, the same “review style” was applied as well on papers of other authors - we did not have the time to check this.

In order to demonstrate these severe incriminations, some unambiguous examples will be shown in this manuscript. We have already recognized numerous further examples, including obvious mistakes of the reviewer or ridiculous recalculations concerning papers, which we know very well. However, we did not yet have the time to work out all these examples.

Moreover, the review does not represent the present state of the art. At the end of this

manuscript, we will point out some problems, which complicate the understanding and the interpretation of the available experimental data in the Np(V) carbonate systems. Although these problems were already discussed in papers of Kim and coworkers [95NEC/FAN, 95FAN/NEC, 96FAN/NEC] and also by other authors [95NOV/ROB, 96RUN/KIM, 97NOV/ALM, 98ALM/NOV], the reviewer might not have understood these papers. Some of these problems are closely related to the shortcomings and simplifications of the SIT approach used in the NEA-TDB reviews for the calculation of activity coefficients. This concerns also auxiliary data used in the NEA-TDB for the calculation of carbonate ion trace activity coefficients in NaClO<sub>4</sub> solutions.

Example 1

This first example demonstrates the attempt of the reviewer (P. Vitorge) to discredit our work by claiming that there are inconsistencies and the published data are therefore unacceptable. This statement is repeated several times throughout the review. The example concerns aqueous Np(V) carbonate complexes, and our measurements with two different methods differ 0.2 log units, which is in general considered as fair agreement and not as inconsistency.

In the review of [91KIM/KLE] (Appendix A), the reviewer writes:

*page 808, lines 1 - 7:*

*The spectra of Np(V) carbonate complexes were also reported and were used later [94NEC/RUN] to calculate the formation constants of two Np(V) carbonate complexes. The spectra were in accord with those previously found by Riglet [90RIG]. The reported value of  $\beta_1$  was not consistent (within the uncertainties estimated by the authors) with the value measured by the solubility technique, and the same was true for the  $\beta_2$  values reported in [94NEC/RUN]. This inconsistency was pointed out by the authors, but was not explained.*

An almost identical comment is given in section 12.1.2 (page 255, lines 1 - 7) the reviewer then concludes:

*page 255, lines 7 - 10:*

*There appears to have been a problem with this work, but there is not enough experimental information to reinterpret these spectrophotometric measurements. These values are not used in the present review in selection of the values for the complexation constants.*

In order to emphasize the “miserable” work in [94NEC/RUN], the reviewer repeats in the review of paper [96CLA/CON] (Appendix A):

*page 841, lines 29-32:*

*.... possibly as described by Neck et al. [94NEC/RUN] (However, the spectrophotometric results of that publication were not particularly accurate and were not used in the final data assessment in the present review. See the discussion of [94NEC/RUN])*

Thus criticized, the reader must expect strong inconsistencies and inaccuracies among the  $\log \beta_1$  and  $\log \beta_2$  values reported in [94NEC/RUN] for 0.1 M NaClO<sub>4</sub> solution. Actually the review concerns the following data:

solubility:	$\log K_1 = 4.58 \pm 0.04$	$\log K_2 = 6.60 \pm 0.07$	[94NEC/RUN]
spectroscopy:	$\log K_1 = 4.38 \pm 0.04$	$\log K_2 = 6.4 \pm 0.3$	[94NEC/RUN]

Indeed, the  $\log K_1$  values do not agree within the underestimated range of uncertainty. However, readers with experimental experience in the field of aquatic actinide chemistry might consider differences of 0.2 log units (for two different experimental methods) as fair agreement, not as inconsistencies. In order to prevent these readers from doing so, the reviewer does not give the numerical values for comparison, well knowing that only few readers will look for these values in the original paper or in the comprehensive Table 12.4 (p.245 - 251).

On the other hand, it is somewhat surprising that there is no corresponding critical comment on the solubility and spectroscopic studies of Vitorge and coworkers [86GRE/ROB, 90RIG], which include 2 - 3 times larger inconsistencies (c.f. Table 12.4 and Figs. 12.2 - 12.4), e.g. for the consecutive complexation equilibrium  $\text{NpO}_2(\text{CO}_3)_2^{3-} + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$  in 3 M  $\text{NaClO}_4$  (from Table 12.4, p.247):

solubility:	$\log K_3 = 2.31 \pm 0.14$	[86GRE/ROB]
spectroscopy:	$\log K_3 = 2.9 \pm 0.2$	[90RIG]

Quite in contrast to the disregarded “inaccurate” data reported in [94NEC/RUN], the results in [86GRE/ROB, 90RIG] are considered as most reliable and selected for the evaluation of ion interaction coefficients and equilibrium constants at  $I = 0$ . This reflects the reviewer’s (Vitorge’s) very personal interpretation of the guidelines for NEA-TDB reviews.

## Example 2

Np(V) carbonate complexes; statement on page 256

*page 256, lines 27 - 29:*

*Two different values of  $K^\circ_3$  (based on the same data) were reported by Kim et al [91KIM/KLE, 94NEC/KIM], and no explanation was offered for this inconsistency.*

This short sentence, which is again nothing but an attempt to discredit our work, includes the following incorrect citations or statements:

- 1.) We never evaluated consecutive constants  $\log K_n$ , neither from our solubility data in [91KIM/KLE, 94NEC/KIM, 94NEC/RUN] nor in our later review paper [95FAN/NEC], but formation constants  $\log \beta_n$ . (Since there are generally enough and accurate data in the pH-range, where  $\text{NpO}_2^+$  is the predominant species, it is much more convenient to evaluate the solubility product and  $\log \beta_n$  instead of  $\log K_n$  values - analog to the methodology applied in the NEA review on the U(VI)-carbonate system [92GRE/FUG])
- 2.) The cited report [94NEC/KIM] does not include any extrapolation to  $I = 0$ , but only experimental data in 5 M NaCl and in 5 M NaClO<sub>4</sub>. Extrapolations to  $I = 0$ , either with the SIT or Pitzer equations, are given in other papers [94NEC/RUN, 95FAN/NEC].
- 3.) The  $\log \beta_n$  values evaluated in [91KIM/KLE, 94NEC/RUN, 95FAN/NEC] are not based on the same data as stated by the reviewer. In all our papers, it is well noted, which data are used for the evaluation of constants at  $I = 0$  (c.f. table below). And it is most trivial that a different set of experimental data consequently leads to different values at  $I = 0$ . Further, it is well-known, that particularly for highly charged ions like  $\text{NpO}_2(\text{CO}_3)_3^{5-}$ , SIT and Pitzer equations may give different activity coefficients in the very low ionic strength range.
- 4.) In order to obtain an impression on the magnitude of the “inconsistencies” (which are of course not given numerically by Vitorge), the evaluated constants  $\log \beta_n$  are listed in the table below. Moreover, from the comparison with the values selected by Vitorge, the following question arises: If all the papers of the “Kim group” are that inconsistent and contain so many mistakes, how is it then possible that Vitorge selects the same constants (within the range of uncertainty of those given in [91KIM/KLE, 94NEC/RUN, 95FAN/NEC]) ?

Table 1. Formation constants  $\log \beta_n$  of Np(V) carbonate complexes

Ref.	Method	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	exp. data used
[91KIM/KLE]	SIT	$5.04 \pm 0.06$	$6.59 \pm 0.09$	$5.73 \pm 0.17$	$\text{NaClO}_4$ <sup>a)</sup>
[94NEC/RUN, 95FAN/NEC]	SIT	$4.83 \pm 0.15$	$6.55 \pm 0.23$	$5.54 \pm 0.09$	$\text{NaClO}_4$ <sup>b)</sup> ;
[95FAN/NEC]	Pitzer	$5.03 \pm 0.06$	$6.47 \pm 0.14$	$5.37 \pm 0.36$	$\text{NaClO}_4$ + $\text{NaCl}$ <sup>c)</sup>
Vitorge's review	SIT	$4.96 \pm 0.06$	$6.53 \pm 0.10$	$5.50 \pm 0.15$	$\text{NaClO}_4$

<sup>a)</sup> exp. data (0.1 - 3.5 m  $\text{NaClO}_4$ ) from [91KIM/KLE]

<sup>b)</sup> exp. data (0.1 - 3.5 m  $\text{NaClO}_4$ ) from [83MAY, 86GRE/ROB, 85BID/TAN, 85INO/TOC, 90NIT/STA, 90RIG, 91KIM/KLE, 94NEC/RUN, 94MEI]

<sup>c)</sup> exp. data (0.1 - 6.5 m  $\text{NaClO}_4$  and 0.1 - 5.6 m  $\text{NaCl}$ ) from [83MAY, 86GRE/ROB, 85BID/TAN, 85INO/TOC, 90NIT/STA, 90RIG, 91KIM/KLE, 94NEC/RUN, 94MEI, 94NEC/KIM, 94RUN/KIM]

### Example 3

#### Mixed Np(V) hydroxide-carbonate complexes

*page 241, lines 3 - 7:*

*Varlashkin, Begun and Hobart [84VAR/BEG] reported ... These results were later confirmed by Riglet [90RIG] and Vitorge and Capdevila [98VIT/CAP], and interpreted as evidence of the formation of mixed Np(V) hydroxide-carbonate complexes.*

In this section the reviewer does not mention that, extending the former qualitative studies, we identified and quantified two ternary complexes,  $\text{NpO}_2(\text{OH})(\text{CO}_3)_2^{4-}$  and  $\text{NpO}_2(\text{OH})_2(\text{CO}_3)^{3-}$  [97NEC/FAN]. Our paper is cited later on page 270 and reviewed in Appendix A (discussion of selected references). However, neither the formation constant for the complex  $\text{NpO}_2(\text{OH})_2(\text{CO}_3)^{3-}$  evaluated from the absorption spectra nor the estimate given for  $\text{NpO}_2(\text{OH})(\text{CO}_3)^{2-}$  are mentioned. The following comments are given instead:

*page 270, lines 1 - 4:*

*Neck, Fanghänel and Kim [97NEC/FAN] also recently reported a very similar spectrophotometric study of the dissociation of the carbonate limiting complex in alkaline media; but for the reasons explained in Appendix A, the present review does not rely on their conclusions.*

*Appendix A; page 850, line 37 - page 851, line 4:*

*The predominance diagram shown in this paper (Figure 8 of [97NEC/FAN]) indicated that  $\text{NpO}_2(\text{OH})(\text{CO}_3)^{2-}$  was less than one per cent for the experimental condition of the measurements. This is below the detection limit of their experimental method, and well below the concentration needed to determine its stoichiometry. This is a standard error when stoichiometries are determined only from curve fitting;*

Indeed, it would have been most nonsensical, to evaluate the formation constant for the complex  $\text{NpO}_2(\text{OH})(\text{CO}_3)^{2-}$  from the recorded absorption spectra. However, in our paper ([97NEC/FAN], p.173) it is very clearly pointed out that this complex has not been observed and the constant given for this complex is not derived from absorption spectra, but estimated by interpolation between the known constants in the system  $\text{Np(V)-OH-CO}_3$  in 3 M  $\text{Na(OH/CO}_3/\text{ClO}_4)$ .

The impertinent intention of the reviewer is evident: The reader of this NEA review, who does not read the original paper [97NEC/FAN], should conclude that Neck, Fanghänel and Kim are as stupid to evaluate formation constants from spectroscopic data, even though the contribution of the corresponding species is less than 1 %.

Similarly, the reviewer gives another completely incorrect citation:

*page 270, lines 17 - 21:*

*As suggested by Neck, Fanghänel and Kim [97NEC/FAN] in the qualitative discussion of their spectrophotometric results, formation of  $\text{NpO}_2(\text{OH})_2^-$  and precipitation of a hydroxide compound might be sufficient to explain most of the experimental observations in more alkaline media*

No such statement is given in [97NEC/FAN] ! Just the opposite is the case. It would be absolutely erroneous to assume the formation of  $\text{NpO}_2(\text{OH})_2^-$  under the conditions of our study, i.e. at carbonate concentrations  $> 0.01$  M (c.f. speciation scheme Fig.8 in [97NEC/FAN])

Example 4

Aqueous Np(V) chlorides. In the discussion of aqueous Np(V) chlorides (section 9.2.2.3), the reviewer writes:

*page 179, line 34 - page 181, line 2:*

*Neck, Kim and Kanellakopulos [94NEC/KIM] reported formation constants for the 1:1 and 1:2 complexes, but the ionic strength is high ( $I = 5\text{ M}$ ) and in the absence of precise estimates of the interaction coefficients, the error in the extrapolation to  $I = 0$  will be dominated by the error of our estimates of the ionic interactions. Giffaut [94GIF] observed no significant changes in the visible absorption spectrum of  $\text{NpO}_2^+$  in  $1\text{ M HClO}_4$  and  $4\text{ M NaCl}$ . Hence it would be highly speculative to make a selection on the basis of the existing data.*

The studies at  $I = 5\text{ M}$  (in the cited report [94NEC/KIM]) are extended to  $I = 1, 2$  and  $3\text{ M}$  by analogous experiments in [95NEC/FAN]. This paper also includes the SIT extrapolation to  $I = 0$ . All these data are neither cited in the text nor in Table 9.7 (p.181). Further, the paper [95NEC/FAN] shows absorption spectra in  $0, 1, 2, 3$  and  $5\text{ M NaCl}$  and in  $5, 8,$  and  $10\text{ M LiCl}$  (all at  $\text{pH } 3$ ), i.e. it provides much more spectroscopic information than the paper cited in the review. Finally, the conclusion is given in [95NEC/FAN] (already in the abstract), that there is no evidence for the formation of Np(V) inner sphere chloro complexes, and that the interaction between  $\text{NpO}_2^+$  and  $\text{Cl}^-$  ions should be considered as strong ion-ion interaction without invoking chloro complexes. The quantification of this problem is also reported in [95NEC/FAN]. This paper is well known and the results are frequently cited in the literature.

It appears somewhat strange, that the paper [95NEC/FAN] is not mentioned in the section 9.2.2.3 (Aqueous Np(V) chlorides), although it is cited several times in other sections. The “review“ in Appendix A (discussion of selected references) gives rise to the assumption that the reviewer did not even read this paper. It is restricted to the short statement below, referring to the review of other papers, in which the results discussed above are not included:

*page 836, lines 10-11:*

*[95NEC/FAN] See the discussion of [91KIM/KLE, 94NEC/KIM, 94NEC/RUN] in this appendix.*



Example 5

Solubility of Np(V) carbonates - comment on page 285

*page 285, lines 23 - 25*

*Kim and co-workers [91KIM/KLE, 94MEI, 94NEC/KIM, 94NEC/RUN, 95FAN/NEC, 95NEC/FAN, 95NEC/RUN] reported measurements, that are not in accord with previous work.*

This statement gives the impression that our work differs largely from the results of other authors. A closer look demonstrates that the “disagreement“ is generally very small (  $\sim 0.2$  log units, which is within the range of usual experimental uncertainties), although the data from different authors were obtained under different conditions. In the review of [91KIM/KLE] the reviewer writes:

*page 826, lines 23 - 27*

*The solubility values in 1 M NaClO<sub>4</sub> aqueous solutions were the same as those in [83MAY], and this may be coincidental ... For 3 M NaClO<sub>4</sub> aqueous solutions the results are clearly different from those of Grenthe, Robouch and Vitorge [86GRE/ROB]. The difference is too large to have resulted from pH electrode calibration problems discussed above, but might have resulted from different solid phases being present in the two studies.*

In the figure on the next page (taken from [95FAN/NEC] and [86GRE/ROB]), the solubility data of Kim and co-workers are shown in comparison with previous and later work of other authors. Such a direct comparison of solubility data, which would certainly be more helpful for the reader than the reviewer’s incorrect and contradictory statements, is not shown in the review.

The data shown in the figure below refer to the following papers and experimental conditions:

exp. conditions	pCO <sub>2</sub> = 10 <sup>-3.5</sup> atm	pCO <sub>2</sub> = 0.01 atm or batch experiments
0.1 M NaClO <sub>4</sub>	[91KIM/KLE, 94NEC/RUN]	[94MEI]
1 M NaClO <sub>4</sub>	[91KIM/KLE, 94NEC/RUN]	[83MAY]
3 M NaClO <sub>4</sub>	[91KIM/KLE, 94NEC/RUN]	[86GRE/VIT]
5 M NaCl	[94NEC/KIM]	[94RUN/KIM]



Example 6

Solubility of Np(V) carbonates - review of [94MEI] in Appendix A

*page 829, lines 21 - 28 (review of [94MEI] in Appendix A)*

*As in a previous publication from Kim's laboratory [91KIM/KLE], Meinrath reproduced Vitorge's measurements ... Since original solubility values were reported in the earlier report [91KIM/KLE], and not in the later publication [94MEI], no attempt was made to evaluate Meinrath's results in the present review.*

It is to note that Meinrath was not involved in the Np(V) solubility studies performed in Kim's laboratories (c.f. authors' names of the corresponding papers). The solubility study published in [94MEI] was done independently, at the Japan Atomic Energy Research Institute. And the question must be allowed: How can Meinrath's experiments in 0.1 M NaClO<sub>4</sub> reproduce Vitorge's measurements in 3 M NaClO<sub>4</sub>?

These comments are absolutely inadequate and reveal the reviewer's ridiculous vanity. They clearly demonstrate the reviewer's disinterest to do an objective scientific review:

Example 7

In the review of the paper [94NEC/RUN] in Appendix A, it is stated:

*page 830, line 32 - page 831, line 2*

*In this publication Neck et al. added some new solubility measurements (in 5 M NaCl-carbonate aqueous solutions) to those that had appeared in previous reports ...*

*The presentation of new experimental results included figures showing the transformation of the initial hydrated phase, NaNpO<sub>2</sub>CO<sub>3</sub>(s) into a Na<sub>3</sub>NpO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(s) phase.*

Unfortunately the reviewed paper [94NEC/RUN] does neither contain solubility data in NaCl solutions nor solubility data for Na<sub>3</sub>NpO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>(s). These results are published in the paper [95NEC/RUN], which is however not listed in Appendix A (discussion of selected references).

Example 8

Table 12.4.

Besides wrong citations, e.g. of uncertainties in studies, where originally no uncertainties are given [86GRE/VIT] or vice versa [96RUN/NEU], Table 12.4 contains erroneous citations of experimental data or references (Ref. [91KIM/KLE] does not include data in 3 M NaCl), abstruse recalculations, which change the original published data by more than 0.5 log units (and for some of these recalculations no plausible reasons is given, neither in section 12.1.2 nor in Appendix A). Further, an incorrect citation is found for the solubility product of  $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O(s)}$ :

*Table 12.4, page 248*

*5 M NaCl     $\log_{10} K(I_c) = -9.52^{(h)}$     [94NEC/KIM]*

*<sup>(h)</sup> corrected for chloride complexation (p. 246, bottom).*

Actually this is a direct experimental value, which is by no means corrected for chloride complexation. May be, the notation <sup>(h)</sup> refers to the value of  $\log_{10} K(I_c) = -10.54$  recalculated by the reviewer. However if so, the question would arise, which chloride complexation constants are used for this correction. In section 9.2.2.3 (Aqueous Np(V) chlorides), there was a clear statement that no chloride complexation constant could be selected.

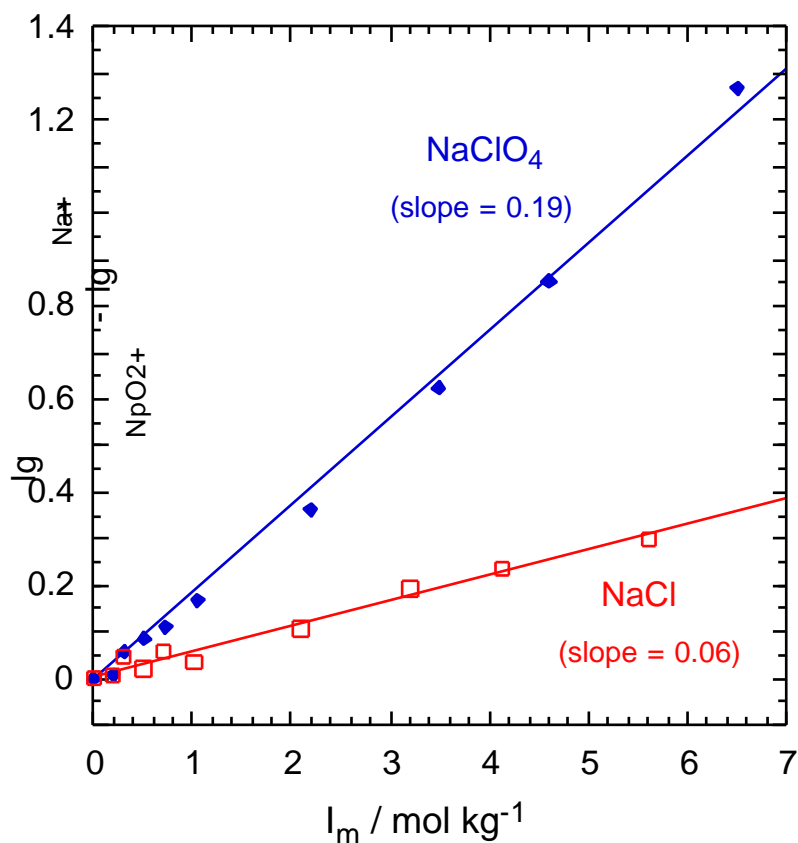
These are just a few examples, which we could recognize at once. Possibly Table 12.4 contains more mistakes.

Example 9

Ion interaction coefficients for the  $\text{NpO}_2^+$  ion

In the report [94NEC/KIM], we published solvent extraction studies, from which the activity coefficient ratio  $(\text{NpO}_2^+)/(\text{Na}^+)$  in 0.2 - 5 M NaCl and  $\text{NaClO}_4$  solutions was determined very accurately. The same results were reported again in the paper [95NEC/FAN], and used to evaluate ion interaction Pitzer coefficients. These Pitzer coefficients were transformed by Vitorge into SIT coefficients (Table A24, p.832 and review of [96RUN/NEU], p.849-850). The more direct and hence more reasonable way to determine  $(\text{NpO}_2^+/\text{Cl}^-) - (\text{Na}^+/\text{Cl}^-)$  and  $(\text{NpO}_2^+/\text{ClO}_4^-) - (\text{Na}^+/\text{ClO}_4^-)$  is shown in the figure below. With the known interaction coefficients for  $\text{Na}^+$  (from the NEA-TDB), those for  $\text{NpO}_2^+$  can be calculated:

$$(\text{NpO}_2^+/\text{Cl}^-) = 0.09 \pm 0.02 \quad \text{and} \quad (\text{NpO}_2^+/\text{ClO}_4^-) = 0.20 \pm 0.03$$



SIT plot of  $\log \left\{ \frac{(\text{NpO}_2^+)}{(\text{Na}^+)} \right\} = (\text{NpO}_2^+/\text{X}^-) - (\text{Na}^+/\text{X}^-)$ , for  $\text{X}^- = \text{ClO}_4^-$  and  $\text{Cl}^-$

These very important experimental data were “reviewed” (and of course not accepted by the reviewer, because they are from Kim and coworkers) with the following sentences:

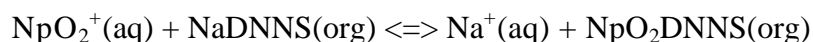
*page 830, lines 21 - 26 (Appendix A, review of [94NEC/KIM])*

*Experimental data of Np(V) liquid-liquid extraction by NaDNNS from 0.2 - 5 M Na(ClO<sub>4</sub>, Cl) aqueous carbonate solutions were also tabulated in this report. These were used by Neck, Kim and Kanellakopulos to estimate Np(V) activity coefficients, however there are difficulties with the interpretation of the authors as explained in the discussion of [94NEC/RUN] (work based on the same experimental data of the same group).*

*page 831, lines 27 - 29 (Appendix A, review of [94NEC/RUN])*

*The interpretation of the liquid-liquid extraction study neglected activity coefficient corrections for the organic phase. These corrections and systematic errors were quite important ...*

Both sentences demonstrate the reviewer’s superficial work and his intention to discredit our work. First of all the studies were of course not performed in aqueous carbonate solutions, which would have been nonsensical, but at constant pH 3, where there is neither hydrolysis nor carbonate complexation. This is clearly documented in both papers [94NEC/KIM, 95NEC/FAN]. Within the liquid-liquid extraction equilibrium studies:



the composition of the organic phase was kept constant, in order to keep constant the activity coefficients of the neutral species in the organic phase. They do not play any role for the evaluation of Pitzer or SIT coefficients for  $\text{NpO}_2^+$  in the aqueous phases.

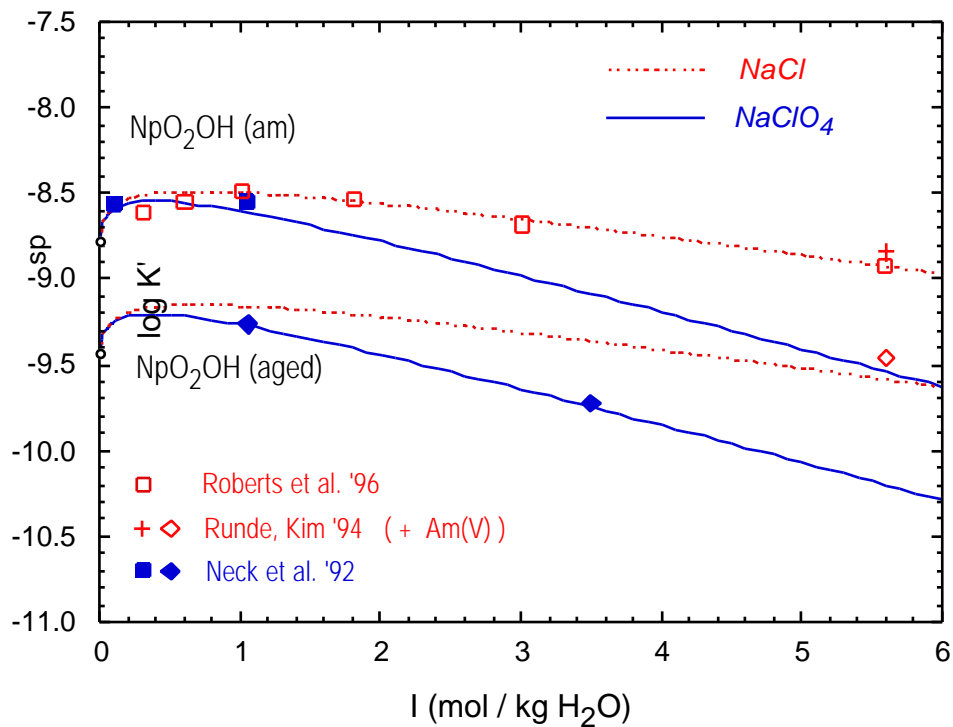
It is to note that the values of  $(\text{NpO}_2^+/\text{Cl}^-)$  and  $(\text{NpO}_2^+/\text{ClO}_4^-)$ , together with  $(\text{Na}^+/\text{OH}^-)$  and the solubility product for  $\text{NpO}_2\text{OH}(\text{am})$  selected in the present NEA review, excellently describe the solubility product of Np(V) hydroxide as a function of the NaCl and NaClO<sub>4</sub> concentrations, respectively (c.f. review of [96ROB/SIL], p.849 and the Figure below).

The value of  $(\text{NpO}_2^+/\text{ClO}_4^-) = 0.20 \pm 0.03$  is in fair agreement with the value selected by Vitorge from measurements on the quasi-reversible redox potential Np(V)/Np(VI):

$(\text{NpO}_2^+/\text{ClO}_4^-) = 0.25 \pm 0.05$ . Vitorge’s value is based on the reasonable assumption that interaction coefficients for  $\text{UO}_2^{2+}$  and  $\text{NpO}_2^{2+}$  should be the same. The same has to be expected for interaction coefficients for  $\text{AnO}_2^+$  ions. The inaccuracy of the redox potential method becomes evident, when the corresponding results for An = U, Np and Pu are compared:

$(\text{UO}_2^+/\text{ClO}_4^-) = 0.26 \pm 0.03$ ,  $(\text{NpO}_2^+/\text{ClO}_4^-) = 0.25 \pm 0.05$   $(\text{PuO}_2^+/\text{ClO}_4^-) = 0.17 \pm 0.05$   
(NEA review [95SIL/BID], page 325; data for Np and Pu from Vitorge’s research group)

Of course, the question, which of the two methods leads to more accurate interaction coefficients ( $\text{NpO}_2^+/\text{ClO}_4^-$ ) might be discussed controversially. However, just disregarding the data from the solvent extraction study in [95NEC/FAN] is certainly not in accord with the guidelines for NEA-TDB reviews.



Solubility products of amorphous and aged Np(V) hydroxide at 25°C as a function of the NaCl and NaClO<sub>4</sub> molality (exp. data from [92NEC/KIM, 94RUN/KIM, 96ROB/SIL]). The ionic strength dependence is calculated (predicted) with ( $\text{NpO}_2^+/\text{Cl}$ ) = 0.09, ( $\text{NpO}_2^+/\text{ClO}_4^-$ ) = 0.20 and ( $\text{Na}^+/\text{OH}^-$ ) = 0.04 [NEA-TDB]

Example 10

Ion interaction coefficients for Np(V) species.

In Table A.24 (page 832), the reviewer deduces “*values of  $\epsilon(\text{NpO}_2^+/\text{ClO}_4^-)$  from the measurements of Kim’s group*”. The only reasonable values given in this table are those derived from the Pitzer parameters reported in [95NEC/FAN, 96RUN/NEU]:

$(\text{NpO}_2^+/\text{ClO}_4^-) = 0.20 \pm 0.03$  and  $0.18 \pm 0.03$ , respectively, which are comparable to the value of  $0.25 \pm 0.05$  from Vitorge (c.f. Example 9). All other values given in this table do not make any sense. We never claimed nonsensical interaction coefficients of  $(\text{NpO}_2^+/\text{ClO}_4^-)$  in the range 0.34 - 0.42, which are “recalculated” by the referee. We published values for the dissolution reaction of  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  and  $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ . These values are not based on “measurements of Kim’s group” alone. They also include the data from other authors. And the reviewer knows very well that analogous calculations, which were based exclusively on the studies declared as reliable by himself (those of Maya [83MAY] and Vitorge [86GRE/VIT] in 1 and 3 M  $\text{NaClO}_4$ ), would lead to almost the same value of . This is of course not mentioned by the reviewer. The reviewer’s subtle intention to discredit our work bare of any scientific reason becomes evident in the following “conclusions”:

*p. 806, lines 17-19*

*The reported parameters [91KIM/KLE, 94NEC/RUN] were also not consistent with those in a later paper [95FAN/NEC] from this group.*

*p. 832, lines 11-16*

*Thus the ionic strength corrections from Kim’s group are not self consistent, and the ones used for solubility products are not consistent with currently accepted  $e$  value. These two inconsistencies could result from several causes: the small systematic errors noted in this appendix, incorrect theoretical methodology, errors in the experimental determination of free carbonate concentrations at high ionic strength or chemical problems with the solid phases.*

We recognized very well the problem of the inconsistencies, when values calculated from  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  solubility products at different  $\text{NaClO}_4$  concentrations or from auxiliary values. And from the perfect consistency concerning the results in the Np(V)-hydroxide system (c.f. Example 9), we also knew very well that this problem does not arise from the activity coefficients of the  $\text{NpO}_2^+$  ion. In our papers [95NEC/FAN, 95FAN/NEC, 95FAN/NEC] it is clearly pointed out that this problem arises from incorrect auxiliary data for the  $\text{CO}_3^{2-}$  ion in  $\text{NaClO}_4$  solutions. (This question will be discussed later in the present manuscript). And the fact that we had several personal discussions on this problem with the reviewer (P. Vitorge) himself, provides further evidence for his impertinent intentions.



A similar, even worse example is included in Table 12.5 (page 253):

Extremely outstanding and unrealistic SIT coefficients  $\beta$  and  $\gamma$  are reported for the papers [95FAN/NEC, 95NOV/ROB]. Since in the original papers, no SIT coefficients are reported at all, these  $\beta$  and  $\gamma$  values are obviously “calculated” by the reviewer. However this is not indicated by footnotes. The experimental data in  $\text{NaClO}_4$  solution applied in [95FAN/NEC] and the evaluated  $\log \gamma_{\text{n}}$  values are essentially the same or similar to those in [94NEC/RUN]. Consequently, the same must hold for the  $\beta$  values, i.e. the reviewer’s calculations (possibly transforming Pitzer into SIT coefficients) must include severe errors. If the reviewer is unable to do such calculations, he should let it be! At least, he should indicate that these “results” were evaluated by the reviewer and not by the authors of the original papers!

Example 11

Solubility product of  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ ;

(discussed on page 284, line 26 - page 288, line 11 and in Fig.12.6, page 289)

From the large number of solubility studies, the reviewer selected those of Maya [83MAY] and Vitorge [86GRE/ROB] (in 1 and 3 M  $\text{NaClO}_4$ , respectively) as the most reliable ones. The results of Kim and coworkers were generally criticized to be not reliable. Solely their solubility product value at  $I = 0$  was included in the reviewer's data selection (which seems to be somewhat arbitrary, if all other data are disregarded). Although the reviewer consedes in another section of the book:

*p.256, lines 9 - 11:*

*... it is possible that the present reviewer did not completely understand the calibration procedure used by Kim et al. ...*

he takes each opportunity to repeat the following reasons for disregarding the results of Kim and coworkers, and also those of former coworkers of Kim (c.f. section 12.1.2 and the corresponding paper reviews in Appendix A):

- (a) systematic errors in pH calibration,
- (b) calculation of  $\log [\text{CO}_3^{2-}]$  or  $\log [\text{OH}^-]$  from measured  $\log [\text{H}^+]$  with auxiliary data, which are inconsistent with the NEA-TDB
- (c) chemical problems with the solid phase

Non of these reasons holds for the studies in 0.1 M  $\text{NaClO}_4$  and 0.1, 1, 3 and 5 M  $\text{NaCl}$ . The dissociation constants of  $\text{H}_2\text{O}$  and  $\text{H}_2\text{CO}_3$  determined by the authors themselves and used to calculate  $\log [\text{CO}_3^{2-}]$  or  $\log [\text{OH}^-]$  from measured  $\log [\text{H}^+]$  are in reasonable agreement (within  $< 0.05$  and  $0.1$  log units, respectively) with well-known and generally accepted literature values and also with the auxiliary data of the NEA-TDB. This was already clearly pointed out in our paper [96FAN/NEC]. (It must be emphasized that reasons (a) and (c) do not hold either for our other studies in 1, 3 and 5 M  $\text{NaClO}_4$ , which will be discussed later.)

The table below (next page) shows the results of 7 solubility experiments, which were performed by 3 different investigators at 4 different institutes: Neck [91KLE/KIM, 94NEC/RUN] (FZK Karlsruhe), Runde (Techn. Univ. Munich and Los Alamos Nat. Lab.) [94RUN/KIM, 96RUN/NEU] and Meinrath [94MEI] (Japan Atomic Energy Research Institute). We now use auxiliary data given in the NEA-TDB for  $(\text{Na}^+/\text{Cl}^-)$ ,  $(\text{Na}^+/\text{ClO}_4^-)$  and

( $\text{Na}^+/\text{CO}_3^{2-}$ ), together with ( $\text{NpO}_2^+/\text{Cl}^-$ ) = 0.09 and ( $\text{NpO}_2^+/\text{ClO}_4^-$ ) = 0.20 or 0.25 discussed in example 9, to calculate the solubility product of  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  at  $I = 0$  (see table below). It becomes evident that (within the range of experimental uncertainties) all these studies lead to a consistent values of  $\log K_{\text{sp}}^\circ$ , in particular if we assume the hydration number of  $x = 3.5$  given in [83MAY]. This demonstrates that in all these studies, even in those at high NaCl concentrations, the solubility data refer to a well-defined unique solid phase.

A serious review would have included these calculations, but the reviewer disregarded all these results for untrue reasons (or for personal animosities concerning the investigators?).

Solubility products of hydrated  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  from studies in 0.1 M  $\text{NaClO}_4$  and in 0.1, 1, 3 and 5 M NaCl (at 20 -25°C)

Ref.	Medium	$\log K_{\text{sp}}$ (molar)	$\log K_{\text{sp}}^\circ (I = 0)$ <sup>a)</sup>	
			x = 0	x = 3.5
[91KIM/KLE, 94NEC/RUN]	0.1 M $\text{NaClO}_4$	-10.28	-10.92	-10.92
[94MEI]	0.1 M $\text{NaClO}_4$	-10.22	-10.86	-10.86
[96RUN/NEU]	0.1 M NaCl	-10.40	-11.05	-11.05
[94RUN/KIM, 96RUN/NEU]	1.0 M NaCl	- 9.77	-10.93	-10.98
[96RUN/NEU]	3.0 M NaCl	- 9.40	-10.67	-10.86
[94RUN/KIM, 95NEC/RUN]	5.0 M NaCl	- 9.61	(-10.83	-11.21) <sup>b)</sup>
[94NEC/KIM]	5.0 M NaCl	- 9.52	(-10.74	-11.12) <sup>b)</sup>

<sup>a)</sup> calculated with ( $\text{Na}^+/\text{Cl}^-$ ) = 0.03, ( $\text{Na}^+/\text{ClO}_4^-$ ) = 0.01, ( $\text{Na}^+/\text{CO}_3^{2-}$ ) = -0.08 (from [95SIL/BID]), ( $\text{NpO}_2^+/\text{Cl}^-$ ) = 0.09 and ( $\text{NpO}_2^+/\text{ClO}_4^-$ ) = 0.20, for x = 0 and 3.5 hydration water molecules, respectively

<sup>b)</sup> at this NaCl concentration the SIT may become inaccurate

Problems concerning the evaluation of thermodynamic data for solid Np(V) carbonates from experimental studies in NaClO<sub>4</sub> solution

In the table below, analogous calculations are done with the published solubility products in NaClO<sub>4</sub> solution. Again the auxiliary interaction coefficients from the NEA-TDB are used (with the exception that  $(\text{NpO}_2^+/\text{ClO}_4^-) = 0.20$  is used, instead of 0.25 as proposed by Vitorge, but this has only a rather limited impact on the calculations.)

In contrast to the observations above in Example 11, the calculated  $\log K_{\text{sp}}^\circ$  values are not consistent. They evidently decrease. The reviewer explains this effect to more or less aged solid phases with different numbers of crystal water molecules. Of course, this possibility cannot generally be ruled out.

Solubility products of hydrated  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  from studies in 0.1 - 5 M NaClO<sub>4</sub>

Ref.	Medium	$\log K_{\text{sp}}$ (molar)	$\log K_{\text{sp}}^\circ (I = 0)$ <sup>a)</sup>	
			x = 0	x = 3.5
[91KIM/KLE, 94NEC/RUN]	0.1 M NaClO <sub>4</sub>	-10.28	-10.92	-10.92
[94MEI]	0.1 M NaClO <sub>4</sub>	-10.22	-10.86	-10.86
[83MAY]	1.0 M NaClO <sub>4</sub>	-10.14	-11.18	-11.23
[91KIM/KLE, 94NEC/RUN]	1.0 M NaClO <sub>4</sub>	-10.10	-11.14	-11.19
[86GRE/ROB]	3.0 M NaClO <sub>4</sub>	-10.56	-11.41	-11.60
[91KIM/KLE, 94NEC/RUN]	3.0 M NaClO <sub>4</sub>	-10.45	-11.30	-11.49
[94NEC/RUN]	5.0 M NaClO <sub>4</sub>	-11.06	(-11.49	-11.87) <sup>b)</sup>

<sup>a)</sup> calculated with  $(\text{Na}^+/\text{ClO}_4^-) = 0.01$ ,  $(\text{Na}^+/\text{CO}_3^{2-}) = -0.08$  (from [95SIL/BID]), and  $(\text{NpO}_2^+/\text{ClO}_4^-) = 0.20$ , for x = 0 and 3.5 hydration water molecules, respectively

<sup>b)</sup> at this NaClO<sub>4</sub> concentration the SIT may become inaccurate

On the other hand, because of (a) the systematic decrease of the  $\log K_{\text{sp}}^\circ$  values and (b) the fact that a comparable decrease of  $\log K_{\text{sp}}^\circ$  was not observed for the different NaCl solutions, it is more likely that the auxiliary data used for the calculation of activity coefficients are not correct. Actually, in our report [Neck, Fanghänel, Kim, FZKA 5599 (1995)], which was later

summarized in the paper [96FAN/NEC], this suspicion was confirmed.

In contrast to our  $\text{H}_2\text{CO}_3$  dissociation constants in 0.1 M  $\text{NaClO}_4$  and in 0.1 - 5 M  $\text{NaCl}$ , determined as accompanying work within our Np(V) solubility studies, our corresponding  $\text{H}_2\text{CO}_3$  dissociation constants in 1, 3 and 5 M  $\text{NaClO}_4$  do not agree with literature values accepted or in accord with the NEA-TDB auxiliary data. It is to note that the same experimental procedure was used in all our experiments, and that the determined dissociation constants of  $\text{H}_2\text{O}$ , were generally in excellent agreement with well-accepted literature values at  $I = 0.1 - 5 \text{ M}$ , in both  $\text{NaCl}$  and  $\text{NaClO}_4$  solution. The latter results confirm that our pH electrode calibration was certainly correct, and not related to systematic errors, as claimed and repeated again and again by the reviewer. We also explained, why so many literature data are incorrect: in all these studies the pH electrode was calibrated only in acidic solutions and then extrapolated to the alkaline range assuming ideal Nernst slopes (59.16 mV / pH unit), whereas the real slopes of commercial glass electrodes are generally somewhat smaller (58.0 - 58.8 mV / pH unit) [96FAN/NEC].

We finally evaluated the activity coefficients and ternary ion interaction Pitzer parameters for carbonate ions in  $\text{NaClO}_4$  solution from the  $\text{H}_2\text{CO}_3$  dissociation constants [96FAN/NEC]. Combining these parameters with those evaluated in [95NEC/FAN] for the activity coefficients of the  $\text{NpO}_2^+$  ion, the value  $\log K_{\text{sp}}^\circ$  for  $\text{NaNpO}_2\text{CO}_3 \cdot 3.5 \text{H}_2\text{O}(\text{s})$  is again calculated from the experimental solubility products (see table below, next page). Now, consistent values at  $I = 0$  are obtained for 12 solubility experiments from 5 different investigators with the solution composition widely varied ( $I = 0.1, 1, 3$  and  $5 \text{ M}$  in both,  $\text{NaCl}$  and  $\text{NaClO}_4$  solutions). The average value is found to be

$$\log K_{\text{sp}}^\circ = -11.08 \pm 0.20 \text{ (2 } \sigma \text{ ) for } \text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s})$$

Using the same activity coefficients, consistent  $\log K_{\text{sp}}^\circ$  values are obtained as well for  $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$  (see [95NEC/FAN]), from experimental results in 1, 3 and 5 M  $\text{NaClO}_4$  and in 5 M  $\text{NaCl}$  [86GRE/ROB, 91KIM/KLE, 94RUN/KIM, 95NEC/RUN].

These calculations provide strong evidence that all the solubility studies listed in the table below refer to a unique, well-defined solid phase. Additional evidence for this arises from several experimental reasons given in [91KIM/KLE, 94NEC/RUN, 95NEC/RUN]. Such experimental reasons are e.g. the reproducibility of the solubility data, when the equilibrium carbonate concentration was increased and decreased again, and the reproducibility when  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  had transformed into  $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$  and then back into  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ , or the long total duration time of about half a year for each experiment.

Solubility products of hydrated  $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$   
in 0.1 - 5 M NaCl and  $\text{NaClO}_4$  (at 20 -25°C)

Ref.	Medium	$\log K_{\text{sp}}$ (molar)	$\log K_{\text{sp}}^{\circ} (I = 0)^{\text{a)}}$ $x = 3.5$
[96RUN/NEU]	0.1 M NaCl	-10.40	-11.08
[94RUN/KIM, 96RUN/NEU]	1.0 M NaCl	- 9.77	-11.10
[96RUN/NEU]	3.0 M NaCl	- 9.40	-11.00
[94RUN/KIM, 95NEC/RUN]	5.0 M NaCl	- 9.61	-11.15
[94NEC/KIM]	5.0 M NaCl	- 9.52	-11.06
<hr/>			
[91KIM/KLE, 94NEC/RUN]	0.1 M $\text{NaClO}_4$	-10.28	-10.94
[94MEI]	0.1 M $\text{NaClO}_4$	-10.22	-10.88
[83MAY]	1.0 M $\text{NaClO}_4$	-10.14	-11.18
[91KIM/KLE, 94NEC/RUN]	1.0 M $\text{NaClO}_4$	-10.10	-11.14
[86GRE/ROB]	3.0 M $\text{NaClO}_4$	-10.56	-11.25
[91KIM/KLE, 94NEC/RUN]	3.0 M $\text{NaClO}_4$	-10.45	-11.14
[94NEC/RUN]	5.0 M $\text{NaClO}_4$	-11.06	-11.08

<sup>a)</sup> calculated with Pitzer parameters given in [95NEC/FAN, 96FAN/NEC]

As a consequence, the conclusions drawn by the reviewer, that the results of Maya [83MAY] and the Kim group refer to a more hydrated solid phase with  $\log K_{\text{sp}}^{\circ} = -11.16 \pm 0.35$  and those of Vitorge [86GRE/ROB] to an aged, less hydrated solid phase with  $\log K_{\text{sp}}^{\circ} = -11.66 \pm 0.50$  (page 287) should urgently be overthought. Even the reviewer states:

*p.286, lines 5 - 7:*

*... However, it is also possible that this work may indicate a need to eventually revise auxiliary data used in the present review (see discussion of [96FAN/NEC] in Appendix A)*

but he does not give any hint, what would be the alternative conclusion.

### Problems due to shortcomings of the SIT approach

But now, if we accept the results and interpretation given in [95NEC/FAN, 96FAN/NEC] another problem arises. This problem is directly related to shortcomings of the SIT approach. According to the results in [96FAN/NEC], the trace activity coefficients of the  $\text{CO}_3^{2-}$  in NaCl and  $\text{NaClO}_4$  solutions above 1 molal are considerably different (see figure, next page). However, these differences cannot be described with the simple SIT approach used in the NEA reviews, because (in contrast to the Pitzer equations) interaction coefficients between ions of the same charge sign are generally set equal to zero. As a consequence, with the SIT approach equal  $\text{CO}_3^{2-}$  trace activity coefficients are calculated for NaCl and  $\text{NaClO}_4$  solutions of equal molality.

In order to demonstrate this kind of shortcoming of the SIT, we worked out two further corresponding examples of well-known different trace activity coefficients, which cannot be described with the SIT:

1) Trace activity coefficients of the  $\text{SO}_4^{2-}$  ion in NaCl and  $\text{NaTcO}_4$  solution, which is quite analog to the problem of  $\text{CO}_3^{2-}$  in NaCl and  $\text{NaClO}_4$  solution.

Unfortunately there are no data for the system Na- $\text{SO}_4$ - $\text{ClO}_4$ , but the  $\text{TcO}_4^-$  ion has properties very similar to those of the  $\text{ClO}_4^-$  ion. The Pitzer parameters in the system Na- $\text{SO}_4$ - $\text{TcO}_4$  are very well known and ascertained by numerous isopiestic and solubility data [Neck, Könnecke, Fanghänel, Kim, J. Solution Chem. 27 (1998), 107 and Neck, Könnecke, Fanghänel, Kim, Radiochim. Acta 83 (1998), 75].

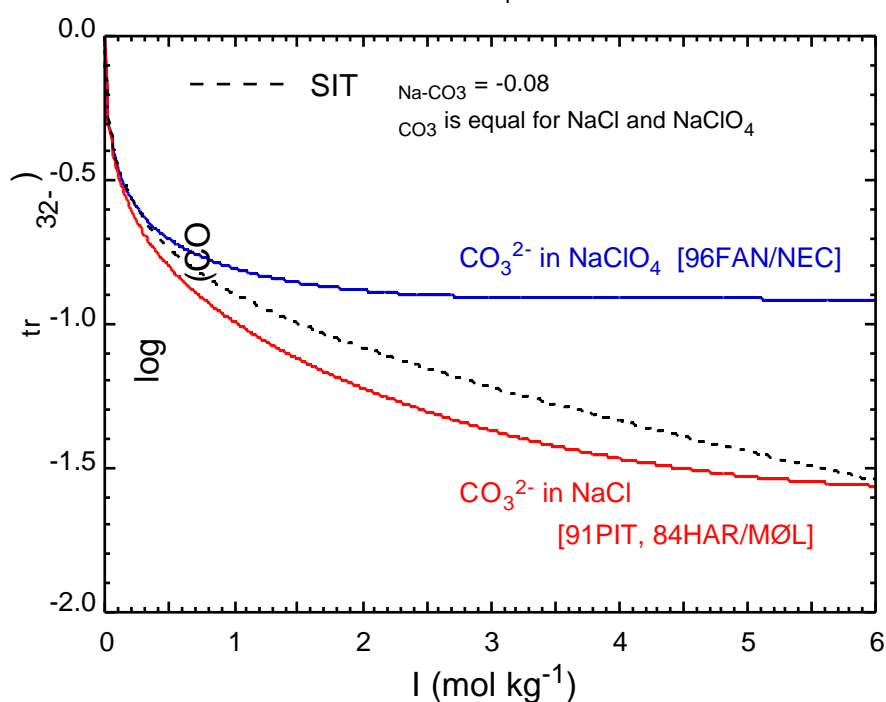
The results are shown on the next page. They show that the corresponding differences in the trace activity coefficients of  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  are comparable, not only qualitatively but also quantitatively.

2) Trace activity coefficients of the  $\text{H}^+$  ion in NaCl and CsCl solution.

According to the SIT, they should be equal, but from emf measurements it is well-known that they are different. The values shown in the corresponding figure are calculated with the Pitzer parameters [91PIT] evaluated from the experimental emf data.

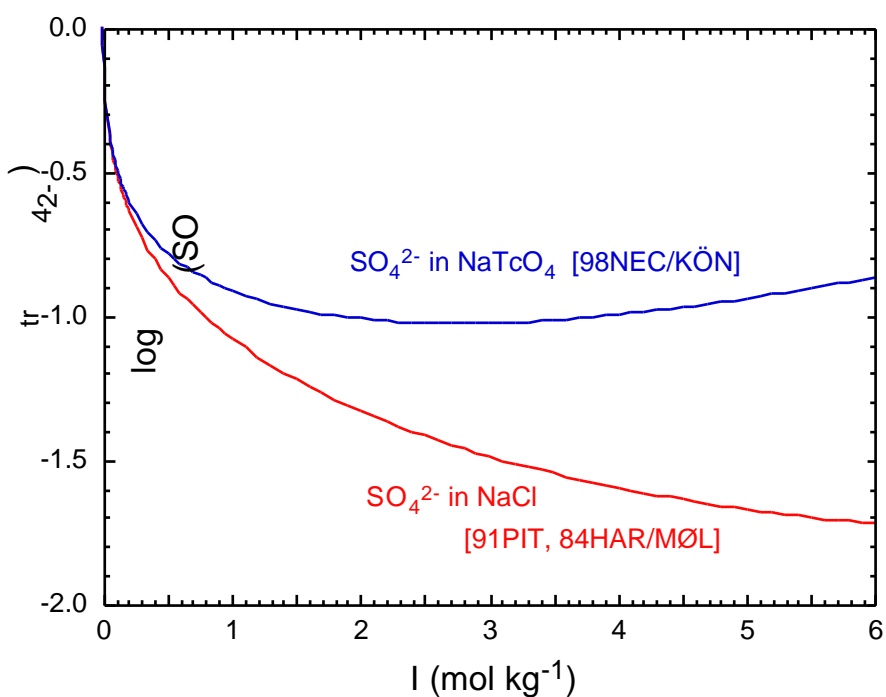
## Trace activity coefficients of the $\text{CO}_3^{2-}$ ion

Comparison between SIT and Pitzer calculations  
for NaCl and  $\text{NaClO}_4$  solutions, 25°C



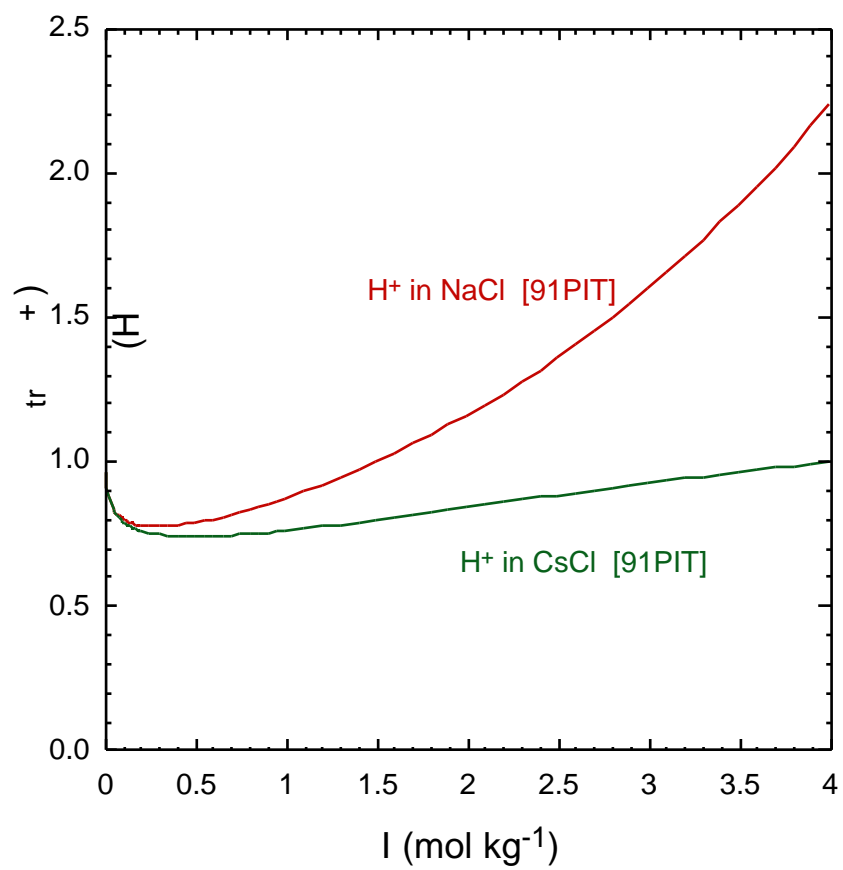
## Trace activity coefficients of the $\text{SO}_4^{2-}$ ion

Pitzer calculations for NaCl and  $\text{NaTcO}_4$  solutions





Trace activity coefficients of the  $\text{H}^+$  ion  
in NaCl and CsCl solutions



Problems in interpreting experimental data on aqueous Np(V) complexes in NaCl solution

Analog problems arise, when the reviewer considered the results of Runde et al.

[96RUN/NEU] on Np(V) carbonate complexation constants in 0.1 - 5 M NaCl.

In the review of [96RUN/NEU] (Appendix A, page 849-850), the reviewer evaluates SIT coefficients between  $\text{Na}^+$  and negatively charged Np(V) carbonate complexes from Runde's data in NaCl solution:

*... which do not seem reliable.... (page 850, lines 11-12)*

The reviewer then blames Runde for applying the Pitzer equations and writes:

*page 850, lines 21-23*

*... The usual scatter of experimental data is in the same order of magnitude as the ionic strength corrections...*

In contrast to the reviewer's statements, the data in [96RUN/NEU] are very well correct. However, again the trace activity coefficients of negatively charged Np(V) complexes are different in NaCl and  $\text{NaClO}_4$  solution, which cannot be described with the simple SIT approach. And as already pointed out in [95FAN/NEC, 96RUN/NEU], this has nothing to do with chloride complexation as supposed in our earlier work [94NEC/KIM, 94RUN/KIM, 95NEC/RUN].

One possibility to overcome this problem would be to calculate only values for the reactions, which are then different for  $\text{NaClO}_4$  and NaCl solution. Another possibility would be to introduce interaction coefficients between ions of the same charge sign, e.g.

$(\text{NpO}_2(\text{CO}_3)_2^{3-}/\text{Cl}^-)$ . However, the latter method would have a severe impact on previous NEA-TDB reviews.

In the past, studies on the ionic strength dependence of dissolution or complexation equilibria were almost exclusively performed in  $\text{NaClO}_4$  solutions. The Np(V)-carbonate system is the first one, for which a large number of experimental data are available in two different electrolyte media. Meanwhile, much more studies on actinide solution thermodynamics are focussed on chloride solutions, because of their relevance for natural systems. This means: the described problems will appear again for other systems with negatively charged complexes (e.g. for U(VI) or Am(III) carbonate and sulphate complexes). Therefore, it does not seem reasonable, just to ignore the problems in the case of Np(V) by disregarding the set of experimental data in NaCl solution.