Comments on actinide carbonate compounds concerning
- NEA-TDB draft of the Np/Pu review
- NEA-TDB II (update of U, Am, Np, Pu, Tc)

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Contents

1. Comments on the experimental studies of Neck and Runde

In the draft of the NEA review on Np/Pu, the results of Kim and coworkers on the solid and aqueous Np(V) carbonates [91KIM/KLE, 94NEC/RUN, 94NEC/KIM, 94RUN/KIM, 95NEC/RUN, 95NEC/FAN, 95FAN/NEC, 96FAN/NEC], were generally critisized to be not reliable. In section 12.1.2 and the corresponding paper reviews in Appendix A (not only in the papers cited above, but also in related papers from other authors) the reviewer takes each opportunity to repeat the following reasons for disregarding the results of Kim and coworkers, and also those of former coworkers of Kim [94MEI, 96RUN/NEU]:

(a) chemical problems with the solid phase
(insufficient knowledge on the equilibrium solid phase)
(b) systematic errors in pH calibration,
(c) calculation of log [CO_3^{2-}] from measured log [H^+] with auxiliary data, which are inconsistent with the NEA-TDB

Statement (a) is absolutely incorrect. In contrast to the reviewer's study (c.f. discussion of [90RIG] in the Np/Pu draft) we had sufficient accurate experimental data and unambiguous experimental proofs for the solubility limiting solid phases (see section 1.1).

Statement (b) is also incorrect as will be shown in section 1.2.

Statement (c) holds only for a part of our studies: for those in 1, 3 and 5 M $NaClO_4$, where the auxiliary data of the NEA-TDB are incorrect as will be shown in the present manuscript. In the studies in 0.1 M $NaClO_4$ and 0.1, 1, 3 and 5 M NaCl, the H_2CO_3 dissociation constants determined and used to calculate log [CO_3^{2-}] from measured log [H^+] agree with well-known and generally accepted literature values and also with the auxiliary data of the NEA-TDB.
Nevertheless, the reviewer disregarded all these results.

Careful reading of our original papers might be sufficient to agree with our arguments.
Several members of the NEA-TDB project groups required additional information and explanations, which hopefully will now be given in this manuscript.
In addition, it has to be stated that the primary intention of any scientific study should be to obtain correct results. The consistency with recommendations of other people or organisations is desirable, but only of secondary importance.

1.1. On the solubility studies with Np(V) carbonates

For the discussion in section 2 of this manuscript, it is important to know that the solubility data in [91KIM/KLE, 94NEC/RUN, 94NEC/KIM, 94RUN/KIM, 95NEC/RUN, 95NEC/FAN, 95FAN/NEC, 96RUN/NEU] refer to well-defined solid phases.
a) hydrated $NaNpO_2CO_3 \cdot 3.5H_2O(s)$ characterised in [77VOL/VIS, 83MAY]
b) $Na_3NpO_2(CO_3)_2(s)$, formed at high carbonate concentration and $[Na^+] \geq 1$ mol/l.

Experimental procedure

All solubility experiments were performed in titration cells (see Appendix 1) under a given CO_2 partial pressure ($10^{-3.5}$ or $10^{-2.0}$ atm) and constant Na^+ concentration of the background solution (0.1, 1, 3 and 5 M $NaClO_4$ or NaCl). The Np(V) solid was precipitated in the titration vessel, and left aging 1 - 2 weeks before the experiment was started. Within the solubility studies in $NaClO_4$ solutions, the pH was varied by adding $HClO_4/NaClO_4$ or $NaHCO_3$/ $NaClO_4$. Equilibration was achieved by bubbling the CO_2/Ar gas mixture through the solution. (The CO_2/Ar stream was preequilibrated with water vapor by bubbling it through a corresponding background solution.) The equilibration between $CO_2(g)$, aqueous carbonate and solid Np(V) carbonate was monitored as a function of time by measuring the H^+ and Np concentrations until these concentrations remained constant. This could last a few days up to 3 weeks, depending primarily on the time needed for the equilibrium between HCO_3^- and CO_3^{2-} in the aqueous phase and pCO_2 in the gas phase.

Maya [83MAY] reported in the experimental section of his paper:
Solid phase $NaNpO_2CO_3 \cdot 3.5H_2O(s)$*. The crystalline compound was prepared ... by addition of* Na_2CO_3 *in a 1:1 mole ratio to a* NpO_2^+ *solution. The gelatinous precipitate initially formed was aged at 25°C for 8 days with slow stirring in the presence of excess* Na_2CO_3 *(0.025 M). This treatment produced a crystalline solid that settled by gravity within a few minutes.*

Exactly the same observation was made in our studies and therefore the solubility experiments were started with a precipitate aged for 1 - 2 weeks.

Solubility limiting solid phases

1) X-ray powder diffraction
The X-ray powder diffraction pattern reported in [94NEC/RUN, 94RUN/KIM, 95NEC/RUN] were taken from a part of the solids used in our solubility studies. The X-ray pattern observed for $NaNpO_2CO_3 \cdot xH_2O(s)$ were all consistent with those reported by Volkov et al. [77VOL/VIS] for $NaNpO_2CO_3 \cdot 3.5H_2O(s)$. The patterns obtained for $Na_3NpO_2(CO_3)_2(s)$ were consistent with the results of Volkov et al. [81VOL/VIS] for that compound. In addition, the report [94RUN/KIM] contains a series of x-ray pattern recorded during the time of solid phase transformation from $NaNpO_2CO_3 \cdot xH_2O(s)$ to $Na_3NpO_2(CO_3)_2(s)$ in 5 M NaCl (see Appendix 2).
In contrast to the results given in [94NEC/RUN, 94RUN/KIM, 95NEC/RUN], Meinrath [94MEI]

reported an other (hexagonal) modification of $NaNpO_2CO_3 \cdot xH_2O(s)$, with a different x-ray pattern. However, he obtained comparable solubility data: the reported solubility constant log K_s in 0.1 M $NaClO_4$ is about 0.1 - 0.2 log units higher than those of [94NEC/RUN] in the same medium and those of [96RUN/NEU] in 0.1 M NaCl.

2) Slope analysis

As shown in [94NEC/RUN], the slopes of the solubility curves (log[Np] vs. log[CO_3^{2-}]) are exactly -1 (not -0.9 ± 0.2 or something like that), over a range of 2 - 2.5 orders of maginude where NpO_2^+ is the predominant aqueous species. The ratio Np : CO_3^{2-} in the solid was exactly 1:1. The presence of solids like $Na_{0.6}NpO_2(CO_3)_{0.8}(s)$ or $Na_{0.72}NpO_2(CO_3)_{0.86}(s)$, as discussed by Vitorge in the NEA review, (p.284 lines 26ff and in Appendix A, discussion of [84VIT, 90RIG]), can certainly be excluded in all our studies. May be such solids are formed as intermediates or as Np(V)-hydroxide-carbonate solid mixtures in the early state of precipitation (where the precipitate is not fine crystalline but hydroxide-like gelatinous) but they are certainly instable and rapidly (within a few day) transformed into a well-defined crystalline $NaNpO_2CO_3 \cdot xH_2O(s)$, with x = 3.5 according to [77VOL/VIS, 83MAY].

In addition, the slope analysis at high carbonate concentration, where the the complex $NpO_2(CO_3)_3^{5-}$ is confirmed spectroscopically as the predominant solution species, again demonstrates that the equilbrium solids are either $NaNpO_2CO_3 \cdot xH_2O(s)$ (slope +2) or $Na_3NpO_2(CO_3)_2(s)$ (slope +1) (see discussion in [91KIM/KLE, 95NEC/RUN]).

3) Solubility data for $NaNpO_2CO_3 \cdot xH_2O(s)$ in 0.1, 1.0 and 3.0 M $NaClO_4$
(from [91KIM/KLE], also reported in [94NEC/RUN])

At first, experiments in 0.1 M $NaClO_4$ were performed in parallel in two titration vessels. After finishing the experiments at I = 0.1 M, the solids in the two vessels (meanwhile about half a year old) were further used for the solubility experiments in 1 and 3 M $NaClO_4$. For this purpose the overstanding solution (I = 0.1 M) was replaced by $HCO_3/NaClO_4$ solutions of I = 1 and I = 3 M. Hence, the solubility data at I = 0.1, 1 and 3 M refer to the same solid phase. And since the solubility data at I = 1 and I = 3 are practically the same as those obtained by Maya [83MAY] and Vitorge [86GRE/ROB] in the corresponding media (c.f. Fig. 1.1), it is evident that the solubility data of these authors refer as well to the same solid, and not to different (more or less aged or hydrated) solids as concluded in the NEA review.

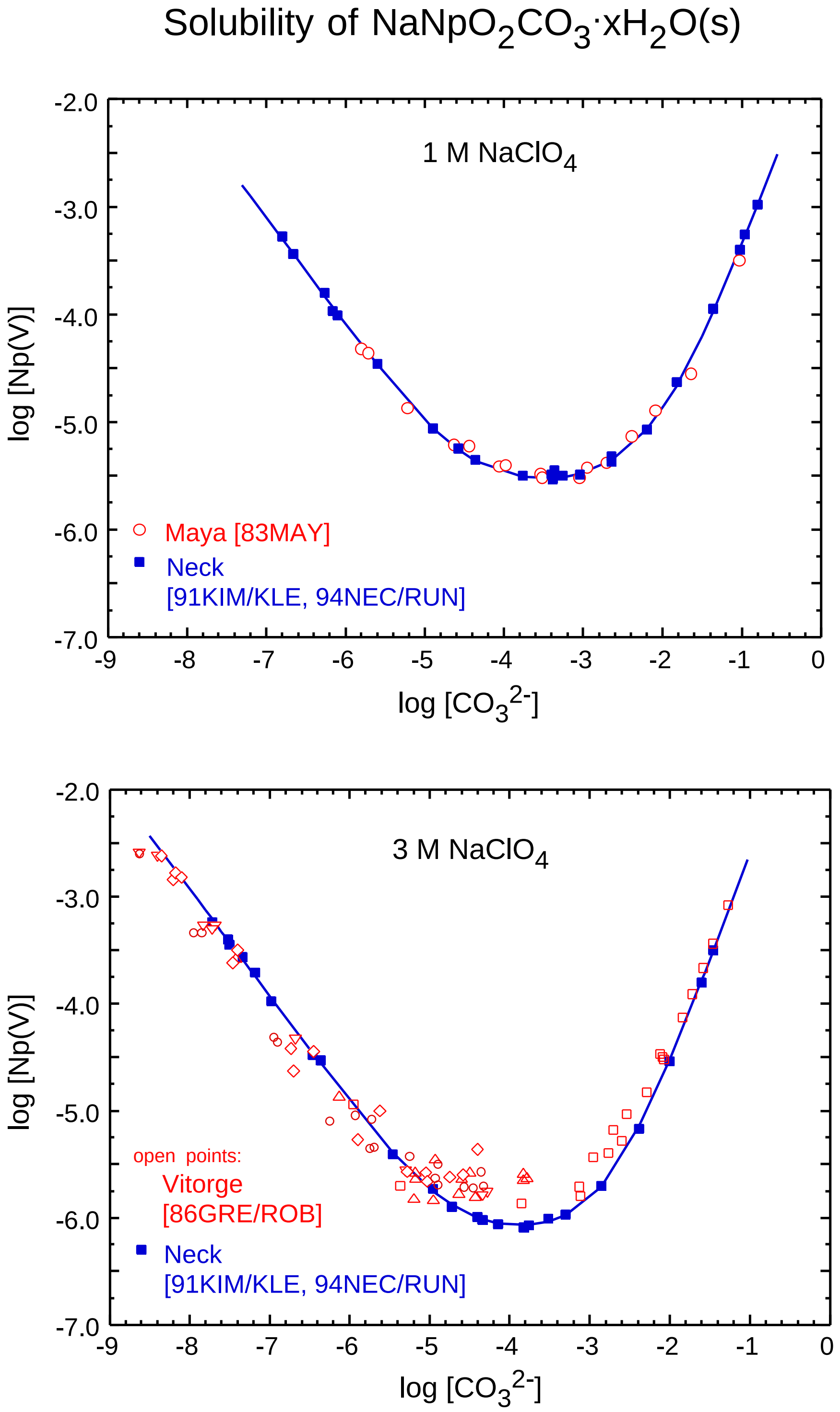

Solubility of $NaNpO_2CO_3 \cdot xH_2O(s)$

Fig. 1.1

4) Reproducibility of the solubility data
In the report [91KIM/KLE], the solubility data in 0.1, 1 and 3 M $NaClO_4$ are listed in the sequence of the measurements (copies of the tables are shown in Appendix 3). From the following observations the formation of different (more or less aged or hydrated) solids of $NaNpO_2CO_3{\cdot}xH_2O(s)$ can definitely be ruled out:
a) The results in 0.1 M $NaClO_4$, measured in parallel in two titration cells are in excellent agreement with each other, i.e. the solids must have been the same.
b) The results in 0.1, 1 and 3 M $NaClO_4$ are reproducible, when pH and carbonate concentration are increased and decreased again, i.e. the solid was not affected.
c) The results for $NaNpO_2CO_3{\cdot}xH_2O(s)$ in 1 and 3 M $NaClO_4$ are reproducible, even after transformation into $Na_3NpO_2(CO_3)_2(s)$ and retransformation into $NaNpO_2CO_3{\cdot}xH_2O(s)$, when pH and carbonate concentration were decreased again, i.e. the retransformation lead again to the same solid $NaNpO_2CO_3{\cdot}xH_2O(s)$,.

These are 4 unambigious proofs that the solubility data refer to well-defined solids.
In Vitorge’s review of the Np(V) carbonates, not a single sentence was written on these efforts and solid phase characterizations, neither in chapter 12.1.2 nor in the Appendix A (discussion of references). Quite in contrast, he states and repeats several times that Kim and coworkers might have had chemical problems with the solid phase.

Accuracy of solubility measurements

In Vitorge’s review and also in the comments of Robert Lemire (in his reply to our letter), there were doubts on the solubility data given in our papers [91KIM/KLE, 94NEC/RUN, 94NEC/KIM, 94RUN/KIM, 95NEC/RUN], because they are less scattered than expected.
In order to achieve such accurate data, great efforts are necessary. And actually great efforts were made, not only in our studies but also by other authors (e.g. [83MAY, 94MEI]), who also reported Np(V) carbonate solubility data of comparable high accurcy. Some of these efforts (considered as self-evident and not reported in detail in our papers) are given below.
In general, there are two important points:

1) The analyical methods to determine the concentrations of interrest. The analytical method to determine the Np-237 concentration will be discussed below. The methods used to determine the H^+ and CO_3^{2-} concentrations will be described seperately in section 1.2

2) In a phase equilibrium study, it is urgently necessary to ascertain that the measured data actually refer to the equilibrium state. Non-equilibrium data are useless for the determination of thermodynamic quantities.

Determination of the Np-237 concentration

The accurate determination of the Np-237 concentration requires certain efforts and is not trivial. In the NEA review possible uncertainties are underestimated:

p.255, lines 27-31
Another potential problem is that ... can result in a constant minimum total ^{237}*Np(V) solubility, which is not far from the usual analytical detection limits (for* α*- or* γ*-spectrometry or liquid scintillation methods); however this does not seem to have caused any difficulties in any of the publications cited here.*

In contrast to this statement, insufficient analytical facilities might very well have lead to inaccurate data or data scattering. It is a more probable reason for the data scattering in the solubility experiments of Vitorge [86GRE/ROB] or Lemire et al.[93LEM/BOY] than the presence of different solid phases (which is the explanation given by the reviewer).
Lemire et al. [93LEM/BOY] mainly applied α-spectrometry (efficiency < 20%). The analytical procedure included several steps (reduction to Np(IV), extraction, back-extraction) to avoid further reduction of the efficiency due to sorption effects, if the dried aliquots contain large amounts of salt from the electrolyte medium. It is not surprising, if this analytical procedure leads to scattered data, in particular for Np concentrations < 10^{-5} M, close to or at the detection limit of α- and γ-spectrometry.

Liquid scintillation α-counting (efficiency: 100%) is certainly much more appropriate to determine the concentration of Np-237. However, the LSC α-spectrum of Np-237 overlaps with the β-spectrum of the short-lived daughter nuclide Pa-233 ($t_{1/2}$ = 27 days, β-decays with maximum energies of 0.3 and 0.6 MeV) - see Appendix 4. The accurate determination of the Np-237 concentration requires an additional α/β discrimination for the counts from Pa-233. The ratio of the counts from Np-237 and Pa-233 can vary in a wide range and is not reproducible. The extremly small traces of Pa can be sorbed on the glass surface, on the Np(V) solid or dissolved as carbonate complexes. From the experience in our studies we know that particularly in the solubility minimum range, the ratio of ^{233}Pa-β-counts : ^{237}Np-α-counts can be very high. If the LSC measurements are not corrected by discriminating the β-radiation from Pa-233, the Np(V) solubility will be considerably overestimated. The analytical method used by Vitorge et al. is neither mentioned in the paper [86GRE/ROB] nor in Riglet's thesis [90RIG]. May be, at the time Vitorge performed the solubility experiments shown in Fig.1.1 (before 1984), he did not have the analytical facilities necessary to record LSC spectra for α/β discrimination.

Procedure to ascertain the equilibrium state

Within the solubility studies in $NaClO_4$ solutions, the pH was varied by adding $HClO_4$/$NaClO_4$ or $NaHCO_3$/$NaClO_4$. The excess of total carbonate (compared to that in equilibrium with $pCO_2 = 10^{-3.5}$

atm) was driven out of the solution by bubbling the CO_2/Ar gas mixture through the solution: $HCO_3^- + H^+ \rightarrow CO_2(g)\uparrow + H_2O$

When the equilibrium between HCO_3^- and CO_3^{2-} in the aqueous phase and pCO_2 in the gas phase is reached, the H^+ concentration remains constant. And when the dissolution equilibrium of the Np(V) carbonate solid is reached, the Np concentration remains constant as well. In our studies, the equilibration procedure was continued until the H^+ and Np concentrations remained constant within about ±0.02 logarithmic units.

That means: each of the given solubility data represents the final, asymptotically reached equilibrium value of a series of H^+ and Np measurements as a function of time! This explains why our data show such a small scattering. Of course, such an experimental procedure requires large efforts and a very long time compared to other methods like closed system batch experiments at given total carbonate concentration. However, it has the following advantages:

1) One can very well ascertain that the equilbrium state (solid phase <=> aqueous phase <=> gas phase) is reached.

2) One can very well recognize, from jumps in the Np concentration, when the solid phase is aging (e.g. NpO_2OH(am -> aged), c.f. Figs. in [91KIM/KLE, 92NEC/KIM]) or transformed (e.g. $NaNpO_2CO_3 \cdot xH_2O(s) \rightarrow Na_3NpO_2(CO_3)_2(s)$, c.f. Figs. in [91KIM/KLE, 94RUN/KIM, 95NEC/RUN]).

1.2. On the determination of the H^+, OH^- and CO_3^{2-} concentrations

At first it is to state that for the evaluation of conditional equilibrium constants in solutions of constant background medium, the correct concentrations of the reactands involved (H^+, OH^- and CO_3^{2-}) are needed (not pH or activity coefficients). All our experimental studies of concern [92NEC/KIM, 91KIM/KLE, 94NEC/RUN, 94NEC/KIM, 94RUN/KIM, 95NEC/RUN, 95NEC/FAN, 96FAN/NEC] were performed in a constant background medium (0.1, 1, 3 and 5 M $NaClO_4$ or NaCl). In order to avoid repetition for all these background media in the following sections, the methods used to determine the concentrations of H^+, OH^- and CO_3^{2-} are explained for the example of 3 M $NaClO_4$ as background medium. The same methods are applied in all other cases.

Calibration of pH electrodes and determination of the H^+ and OH^- concentrations

Method A

The pH electrodes are calibrated in the acidic and alkaline range, with solutions of known H^+ and OH^- concentrations in the same background medium as used for the experiments.

Example:

Experiment at constant ionic strength (3 M $NaClO_4$):

Calibration with a) x M $HClO_4$ / (3 - x) M $NaClO_4$; x = 0.1 - 0.001

b) x M NaOH / (3 - x) M $NaClO_4$; x = 0.1 - 0.001

The ion products of water needed to calculate $\log[H^+]$ from $\log[OH^-]$ (or vice versa) in NaCl or $NaClO_4$ solutions are well known (e.g. auxiliary data of the NEA-TDB). However, the electrode calibration has to be permanently checked during the experiment, and the handling of NaOH solutions under inert gas atmosphere requires certain efforts. Therefore we applied also Method B.

Method B

We use standard pH buffer solutions (related to NIST or NBS) for calibration. This requires an additional correction to obtain the concentration $\log[H^+]$, because the liquid junction potential when calibrating with standard buffer solutions of low ionic strength differs from the liquid junction potential when measuring the test solutions (e.g. in 3 M $NaClO_4$). The value of $pH_{(exp)}$ measured in the test solutions is related to the H^+ concentration by

$$-\log[H^+] = pH_{(exp)} + A$$

with

$$A = \Delta pH + \log \gamma H^+$$

The term A represents a correction for the differences in liquid junction potentials (ΔpH) and the trace activity coefficient of H^+. It has to be determined experimentally by measuring $pH_{(exp)}$ in solutions with known H^+ concentration (x M $HClO_4$ / (3 - x) M $NaClO_4$). After that correction,

Methods A and B lead to the same values of log$[H^+]$.
It is to note that Method B is applied by very many research groups, not only in the studies of Neck and Runde, but also by Rai et al. [91FEL/RAI, 97RAI/FEL] and by other groups in the USA and in Japan.

Unfortunately, our earlier publications [92NEC/KIM, 91KIM/KLE, 94NEC/RUN] contain illustrations of solubilities as a function of pH (-log of the H^+ activity), which is calculated from the concentration log$[H^+]$ by assuming equal trace activity coefficients for H^+ and OH^- ions. Similarly this assumption is used to estimate the "real" shift ΔpH caused by the liquid junction potentials. Indeed this assumption is not consistent with the SIT or Pitzer splitting conventions, which might be confusing to the reader and to the NEA reviewers. However, it must be emphasized that this assumption or convention is completely irrelevant for the calculation of the conditional equilibrium constants, because the equilibrium constants are, of course, calculated from the concentrations log$[H^+]$ and log$[OH^-]$, not from activities.

Question: correct or incorrect values of log $[H^+]$ and log $[OH^-]$?

1) Combining calibration Methods A and B, it is possible to evaluate the ion product of water ($\log K'_w$) in the given background solution, because the value of ΔpH is given by the background electrolyte concentration and the same for acidic and alkaline solutions. The details are given in our papers (e.g. in [92NEC/KIM, 96FAN/NEC]).
It is to note that all our values of $\log K_w$ (in 0.1, 1, 3 and 5 M $NaClO_4$ and in 0.1, 1, 3 and 5 M NaCl) agree well with generally accepted literature data, with those calculated from Pitzer parameters [91PIT] and with $\log K_w$ according to SIT and NEA-TDB. It is hence obvious that we applied a correct methodology to determine the concentrations of H^+ and OH^-.

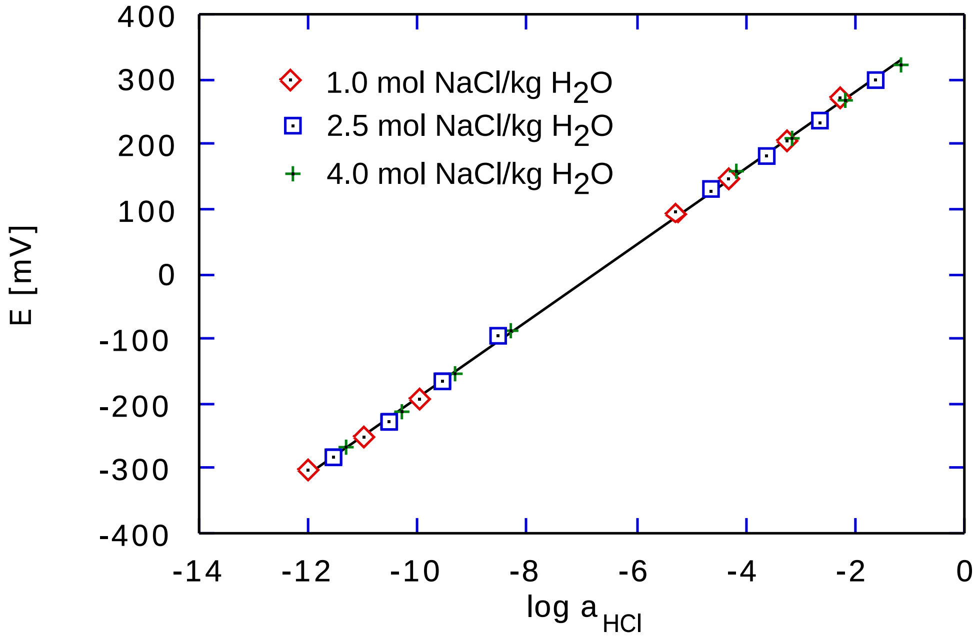
2) Example: log$[OH^-]$ in the studies on Np(V) hydrolysis
If we use our calibrated pH electrode to measure a solution of 0.01 M NaOH / 2.99 M $NaClO_4$, then the final result must be: log$[OH^-]$ = -2.00 (± uncertainty). And if we use the same electrode and the same pH-meter and measure the same emf value in a solution of a solubility experiment in 3 M $NaClO_4$, it certainly follows again that log$[OH^-]$ = -2.00 (± uncertainty). We cannot accept any other interpretation.

3) Comment on objections (Pierre Vitorge, Robert Lemire) concerning possible carbonate contamination in NaOH calibration solutions.
As demonstrated in our experiments on Np(V) hydrolysis [92NEC/KIM, 91KIM/KLE, 94RUN/KIM], we are certainly able to keep a possible carbonate contamination below 10^{-5} mol/l. (At this carbonate concentration the Np(V) speciation is already significantly affected by carbonate complexation.) And it is a simple calculation exercise, how $\log[OH^-]$ is affected by carbonate contamination due to uptake of CO_2(g). Example: even if we assume a considerably overestimated carbonate contamination of 10^{-4} mol/l in a 0.01 M NaOH / 2.99 M $NaClO_4$ solution, then $\log[OH^-]$ is decreased from -2.00 to -2.01. Even in this “worst case“, the error would be less than the general uncertainty of pH measurements.

Comments on other pH calibration procedures

In the literature, pH glass electrodes are often calibrated according to Method A, however, only in the acidic range, and then extrapolated to the alkaline range by assuming an ideal Nernst slope of (59.16 mV/pH unit). In the neutral and alkaline range this can lead to errors up to 0.1 - 0.2 units in $\log[H^+]$, because commercial glass electrodes do not have ideal slopes. Their slopes are slightly lower (58.0 - 58.8 mV/pH unit). We observed this deviation for ROSS electrodes, independent of using calibration method A or B. We also asked Orion Co., and they confirmed non-ideal slopes of their glass electrodes. It is to note that this deviation is also observed, if other glass electrodes and half cells without liquid junction are used (Fanghänel et al.[94FAN/KIM] and unpublished results of Grambow et al.). Fig.1.2 shows a typical example of Fanghänel’s investigations. The activity ($\log aH^+ + \log aCl^-$) of 10^{-2} to 10^{-5} m HCl or NaOH in 1.0, 2.5 and 4 m NaCl is measured with a glass electrode and a chloride sensitive electrode without liquid junction. All measured emf data are represented by one straight line with a slope of 58.8 mV / $\log a_{HCl}$.

As discussed in [96FAN/NEC], an incorrect electrode calibration procedure has a severe impact on the NEA-TDB auxiliary data concerning H_2CO_3 dissociation constants and carbonate trace activity coefficients in concentrated $NaClO_4$ solution. Numerous authors (see refs. in [96FAN/NEC]) determined H_2CO_3 dissociation constants in 0.3 - 3 $NaClO_4$ solution, calibrating their glass electrodes only in the acidic range and extrapolating the calibration to the alkaline range under the assumption of an ideal Nernst slope. These constants are consistent with the NEA-TDB auxiliary data. However, they are incorrect by the shift in $\log [H^+]$ caused by the non-ideal Nernst slope.



Measured potential of the liquid junction free cell vs. calculated log(a_{HCl}) for 3 series of standard solutions (slope = 58.8 mV/log(a_{HCl}) ; intercept = 397 mV)

Fig. 1.2
(from [94FAN/KIM])

Vitorge et al. [86GRE/ROB, 90RIG] calibrate their electrodes in the acidic range with $HClO_4$/$NaClO_4$ solutions and in the neutal to alkaline range with carbonate buffers (acceting the NEA-TDB auxiliary data for H_2CO_3 dissociation constants in 3 M $NaClO_4$). By this way, of course they observe an apparently ideal Nernst slope. But actually they just turn in a circle, because the auxiliary data refer to incorrect literature data determined with glass electrodes calibrated only in the acidic range and assuming an ideal Nernst slope.

Vitorge’s comment, that we should have checked our electrodes before use or that we should have used other types of electrodes, and his statement that our pH measurements include systematic errors, are completely inadequate.

H_2CO_3 dissociation constants in NaCl and $NaClO_4$ solution

In the literature, there are very careful experimental studies on the dissociation constants of carbonic acid, usually in diluted chloride solutions (c.f. refs. of Harned et al and others given in [96FAN/NEC]). In these studies, pH or H^+ concentrations are usually measured with Pt/H_2 and chloride electrodes in cells without liquid junction. Based on these studies, the equilibrium constants at $I = 0$ are well known and accepted as standard values (c.f. NBS tables [82WAG/EVA], NEA-TDB [92GRE/FUG, 95SIL/BID], model of Harvie, Møller and Weare for the seawater salt system [84HAR/MØL]).

In NaCl solution, there are numerous experimental data of different type, which allow the determination of the Pitzer parameters in the system $Na\text{-}H\text{-}OH\text{-}HCO_3\text{-}CO_3\text{-}Cl\text{-}H_2O$ at 25°C [91PIT, 84HAR/MØL]. In Fig.1.3 these data are used to calculate the equilibrium constants for the reactions

$$HCO_3^- \iff H^+ + CO_3^{2-} \qquad (\log K_2)$$

and

$$CO_2(g) + H_2O \iff 2\,H^+ + CO_3^{2-} \qquad (\log K_HK_1K_2)$$

as a function of the NaCl molality. Fig.1.3 shows also that the corresponding calculation with the SIT parameters given in the NEA-TDB is almost identical (if we disregard the deviations at high ionic strength). In addition, Fig.1.3 shows that the corresponding conditional constants determined in [94RUN/KIM, 94NEC/KIM] as accompanying work within the Np(V) carbonate solubility studies are in reasonable agreement with the known and generally accepted literature data. This again confirms the experimental procedures (including pH calibration) applied by Neck and Runde.

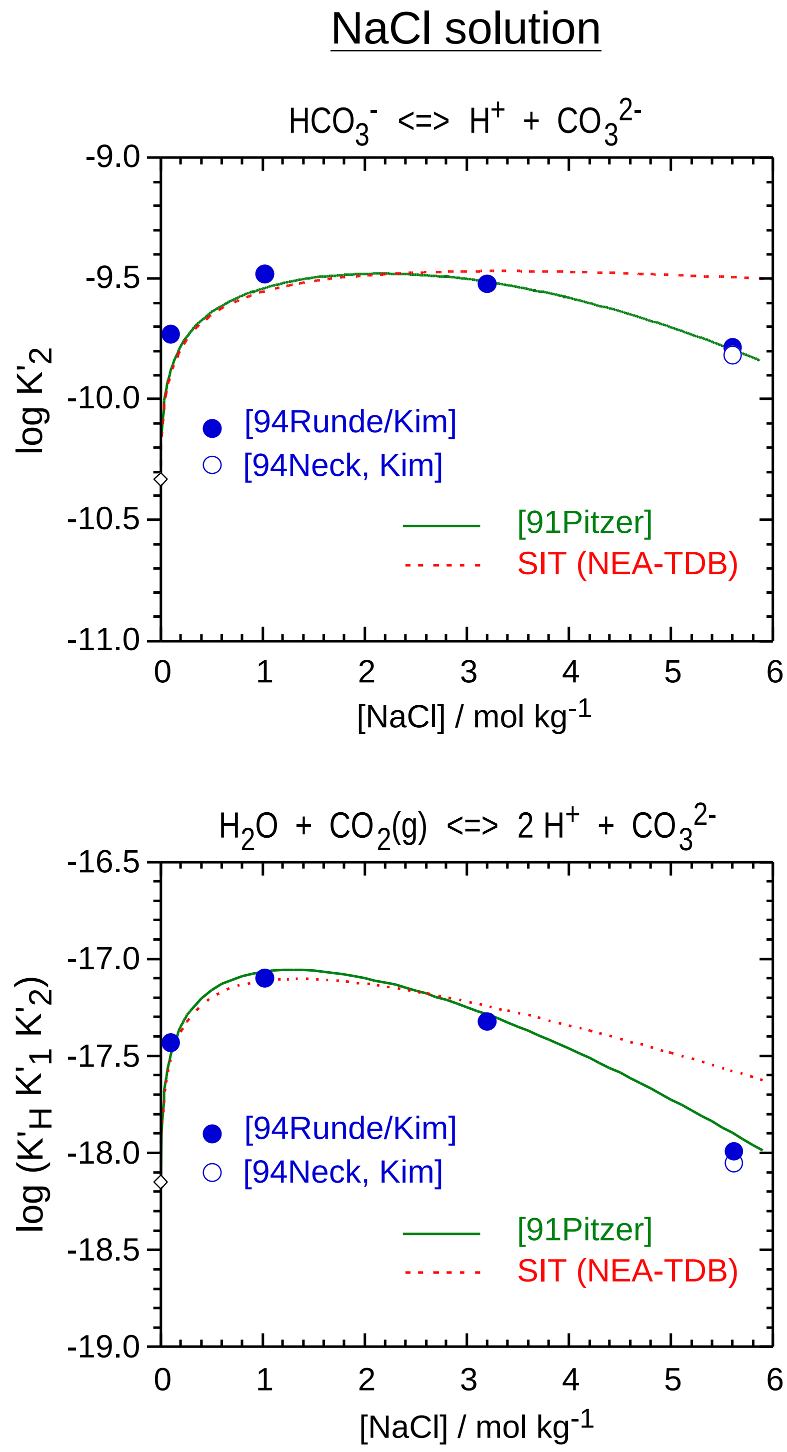

NaCl solution
HCO3- <=> H+ + CO3 2-
log K'2
-9.0
-9.5
-10.0
-10.5
-11.0
0
1
2
3
4
5
6
[NaCl] / mol kg-1
[94Runde/Kim]
[94Neck, Kim]
[91Pitzer]
SIT (NEA-TDB)
H2O + CO2(g) <=> 2 H+ + CO3 2-
log (K'H K'1 K'2)
-16.5
-17.0
-17.5
-18.0
-18.5
-19.0
0
1
2
3
4
5
6
[NaCl] / mol kg-1
[94Runde/Kim]
[94Neck, Kim]
[91Pitzer]
SIT (NEA-TDB)

Fig. 1.3

Fig.1.4. shows the corresponding equilibrium constants in $NaClO_4$ solution. In contrast to the good agreement in NaCl, the experimental results and the Pitzer modeling in [94NEC/RUN, 96FAN/NEC] are strongly conflicting with literature values and with the SIT calculation based on the NEA-TDB parameters (Solely the values in 0.1 M $NaClO_4$, where the effect of SIT coefficients is negligible, are in agreement). However, as already mentioned above and discussed in [96FAN/NEC], except of one log K_2 value, all literature data shown in Fig.1.4 (the references are given in [96FAN/NEC]) were determined with glass electrodes calibrated only in the acidic range, and extrapolated to the alkaline range by assuming ideal Nernst slopes. That means: all these data are incorrect. And even if so many authors obtain comparable results by making the same mistake, a mistake will always remain a mistake.
(The consequences will be discussed in section 2 of the present manuscript.)

This mistake is illustrated in Figs.1.5 and 1.6. The shown real example is taken from our FZKA report (Neck, Fanghänel, Kim, FZKA 5599, June 1995).
Fig.1.5 shows the two different ways of electrode calibration in 3 M $NaClO_4$, either the calibration with both, acidic $HClO_4/NaClO_4$ and alkaline $NaOH/NaClO_4$ solutions (solid line), or the calibration only in the acidic range extrapolated with the ideal Nernst slope (dashed line). In Fig.1.6, the value of log K_2 is determined in a most simple way, by measuring log$[H^+]$ in a solution with the composition:

0.05 M $NaHCO_3$ / 0.05 M Na_2CO_3 / 2.85 M $NaClO_4$
i.e. with log $[HCO_3^-]$ = log $[CO_3^{2-}]$ and hence: log $[H^+]$ = log K_2

If we would have accepted the dashed line for electrode calibration, the value of log $K_2 = -9.64$ would have been obtained, which would have been very well consistent with the literature data and with the auxiliary value of -9.62 from the NEA-TDB. However, the dashed calibration line is not correct - the solid line represents the correct calibration and hence it follows that log $K_2 = -9.81$.

Due to the incorrect pH calibration, the errors in log K_2 are about 0.1 - 0.2 log units. The errors in log $K_HK_1K_2$ are about the double, because two H^+ ions are involved in the equilibrium

$$CO_2(g) + H_2O \Leftrightarrow 2\,H^+ + CO_3^{2-}$$

$NaClO_4$ solution

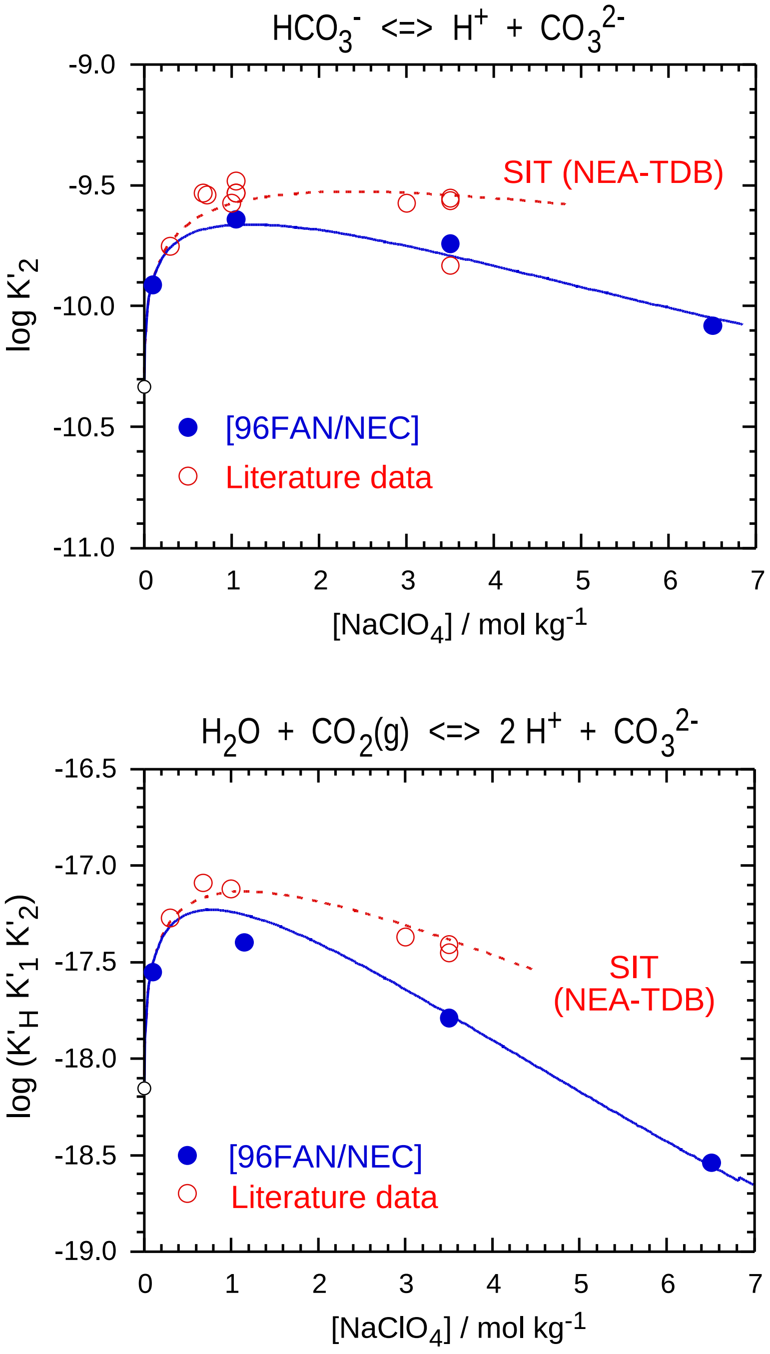


Fig. 1.4

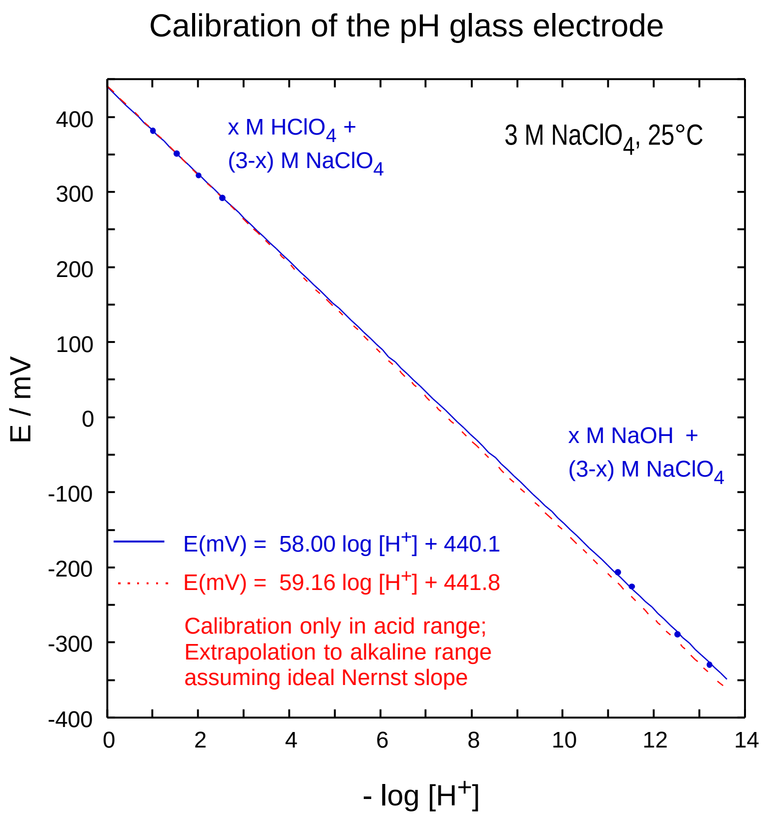

Calibration of the pH glass electrode
x M HClO$_4$ +
(3-x) M NaClO$_4$
3 M NaClO$_4$, 25°C
x M NaOH +
(3-x) M NaClO$_4$
E(mV) = 58.00 log [H$^+$] + 440.1
E(mV) = 59.16 log [H$^+$] + 441.8
Calibration only in acid range;
Extrapolation to alkaline range
assuming ideal Nernst slope
E / mV
400
300
200
100
0
-100
-200
-300
-400
0
2
4
6
8
10
12
14
- log [H$^+$]

Fig. 1.5

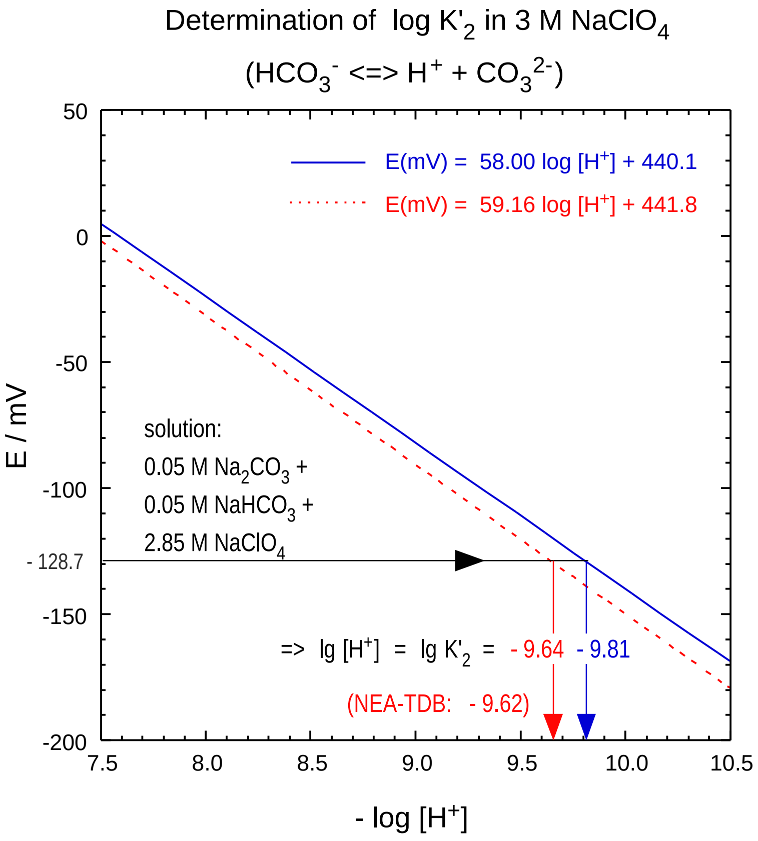

Determination of log K'$_2$ in 3 M NaClO$_4$
(HCO$_3^-$ <=> H$^+$ + CO$_3^{2-}$)
E(mV) = 58.00 log [H$^+$] + 440.1
E(mV) = 59.16 log [H$^+$] + 441.8
solution:
0.05 M Na$_2$CO$_3$ +
0.05 M NaHCO$_3$ +
2.85 M NaClO$_4$
=> lg [H$^+$] = lg K'$_2$ = - 9.64 - 9.81
(NEA-TDB: - 9.62)
E / mV
50
0
-50
-100
- 128.7
-150
-200
7.5
8.0
8.5
9.0
9.5
10.0
10.5
- log [H$^+$]

Fig.1.6

Question: are the carbonate concentrations determined in experimental studies on actinide carbonates correct or incorrect ?

In the Np/Pu draft, the reviewer is irritated, because the Np(V) carbonate solubilities of [91KIM/KLE, 94NEC/RUN] and those of [83MAY] are in good agreement, although considerably different constants are used to calculate the carbonate concentration from the measured values of H^+ concentration:

page 806, lines 23 - 27
The solubility values in 1 M $NaClO_4$ aqueous solutions were the same as those in [83MAY], and this may be coincidental as different values were used for the protonation constants for carbonate ion.

The agreement between the Np(V) carbonate solubilities in [94NEC/RUN] and those in [83MAY] (in 1 M $NaClO_4$) and [86GRE/ROB] (in 3 M $NaClO_4$) is of course not accidently as supposed by Vitorge in the NEA review. This is demonstrated below for a carbonate solution in 3 M $NaClO_4$. Because of the different pH calibration methods, Vitorge et al. (ideal Nernst slope) and Neck (58.0 mV/pH, Fig.1.6) determine a considerably different H^+ concentration. However, because they apply different H_2CO_3 dissociation constants in 3 M $NaClO_4$ (log $K_HK_1K_2$ = -17.62 [86GRE/ROB, 90RIG] and -17.99 [94NEC/RUN]) they finally obtain practically the same (correct) values of log $[CO_3^{2-}]$.

Example: Solution in 3 M $NaClO_4$
equilibrated with atmospherical CO_2(g) partial pressure (log pCO_2 = -3.52)
$[HCO_3^-] = [CO_3^{2-}]$

Vitorge et al.: $\log [H^+] = \log K_2 = -9.62$
$\log [CO_3^{2-}] = -17.62 - 3.52 - 2 \log [H^+] = -1.90$

Neck: $\log [H^+] = \log K_2 = -9.81$
$\log [CO_3^{2-}] = -17.99 - 3.52 - 2 \log [H^+] = -1.89$

Of course, in acidic solutions the calculated carbonate concentrations would be different, e.g. in 0.01 M $HClO_4$/ 2.99 M $NaClO_4$, Vitorge and Neck would measure the same value of $\log[H^+] = -2.00$ but different values of $\log [CO_3^{2-}]$ = -17.14 and -17.51, respectively. However, experiments on actinide carbonates are usually restricted to the limited range of $\log[H^+]$ = -6.5 to -10.5, and the errors in the carbonate concentration remain within the range of other experimental uncertainties.

=> **General comment on "recalculations" of solubility or complexation constants for actinide carbonates**

In the literature and also in the NEA reviews there are often recalculations of original data on solid or aqueous actinide carbonates, and the following reason is given:

The authors XY used the constant of log x to calculate the CO_3^{2-} *concentration from the* H^+ *concentration. However the correct or updated value would be log x'. Therefore the solubility or complexation constant given in the original paper is recalculated using the value of log x' and the following values are obtained ...*

In many cases such recalculations do not correct the original data. Just in contrast - they make them incorrect,

a) if, in a first step, the authors use carbonate auxiliary data to calibrate their pH electrode with carbonate buffers and then, in the second step, they use the same auxiliary data again to calculate $\log[CO_3^{2-}]$ from their measured $\log[H^+]$ concentration.

b) if, in a first step, the authors determine themselves (with their method of pH calibration) the relation between $\log[CO_3^{2-}]$ and $\log[H^+]$ or pH and then, in a second step, they again use this relation to calculate $\log[CO_3^{2-}]$ from their measured values of $\log[H^+]$ or pH.

In both cases, the procedure is internally consistent. The measured values of $\log[H^+]$ may be incorrect (e.g. those of Vitorge et al. in 3 M $NaClO_4$, c.f. example above), but the values of $\log[CO_3^{2-}]$ are correct. The mentioned recalculations are always restricted to the correction of the second step, they never correct the first step, which would be necessary as well. And hence they lead to incorrect results !

2. Erroneous conclusions on actinide carbonates, which arise from limitations/shortcomings of the SIT and erroneous NEA-TDB auxiliary data on trace activity coefficients of the carbonate ion (in $NaClO_4$ solutions above 1 molal)

2.1. General comments on shortcomings of the SIT

2.2. Actinide carbonates: consequences for solubility constants at I = 0

Np(V)	$NaNpO_2CO_3$(s), $Na_3NpO_2(CO_3)_2$(s),
Am(III)	$Am_2(CO_3)_3$(s),
U(VI)	UO_2CO_3(s)

2.3. Proposal to solve the problem of carbonate trace activity coefficients

2.4. Consequences for NEA-TDB reviews

2.1. General comments on shortcomings of the SIT

First of all, it must be emphasized that we do not at all intentend to replace the SIT procedure manifested in the NEA-TDB by introducing Pitzer modelling. (It seems that members of the NEA review groups misinterpreted our objections that way.) However, it is inacceptable that shortcomings and limitations of the SIT are simply ignored, with the consequences that:
(1) erroneous chemical conclusions are drawn and incorrect thermodynamic data are selected because of these shortcomings
(2) correct experimental data are ignored or, even worse, criticized as not reliable, because they are not consistent (or better: cannot be explained) with the simplified SIT approach used in the NEA-TDB.

Limitations of the SIT

1) No triple ion interactions (as included in the Pitzer equations)
=> inaccuracies at high ionic strength (I > 4 m)

2) Debye-Hückel equation with a fixed value of Bå = 1.5
=> inaccuracies at low ionic strength (I -> 0) for ions with high charge |z| > 3

3) Simplification: negligible anion-anion and cation-cation interactions
=> general problem, which makes it impossible to use the same SIT coefficients
for carbonate trace activity coefficients in different electrolyte media

The shortcoming 1) is well-known, and the resulting inaccuracies may be acceptable. The shortcoming 2) can lead to problems and needs further discussion in the future. However these two shortcomings are not the issue of our objections and not further discussed or critisized in the present manuscript. The mentioned objections, which lead to misinterpretations and errors (not inaccuracies, but actually errors!) are exclusively based on shortcoming 3).

Therefore it is now clearly stated once again: the scientific problems do not arise as a question of SIT or Pitzer modelling - they arise from experimental data! In some cases we refer to the Pitzer modelling performed in our papers [95NEC/FAN, 95FAN/NEC, 96FAN/NEC], but this is only done in order to demonstrate the errors coming from the oversimplification of the SIT procedure. At the end of this manuscript, a possible way is shown, how these problems could be solved as well by using an extended SIT formalism, which is not in contradiction to the NEA-TDB guidelines.

According to the results in [96FAN/NEC], where the mixing parameters for CO_3^{2-} and HCO_3^- in $NaClO_4$ solution were evaluated from H_2CO_3 dissociation constants, the trace activity coefficients of the CO_3^{2-} in NaCl and $NaClO_4$ solutions above 1 molal are considerably different (Fig.2.1, next page). 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. (However, these interactions are not zero, and hence included in the binary cation/anion coefficients.) As a consequence, with the SIT approach equal CO_3^{2-} trace activity coefficients are calculated for NaCl and $NaClO_4$ solutions of equal molality.

In order to demonstrate that different carbonate trace activity coefficients in NaCl and $NaClO_4$ solutions are not an artefact arising from erroneous experimental data, we worked out two further corresponding examples of well-known and experimentally well ascertained different trace activity coefficients for an ion dissolved in different media.:

1) Trace activity coefficients of the SO_4^{2-} ion in NaCl and $NaTcO_4$ solution, which is quite analog to the problem of CO_3^{2-} in NaCl and $NaClO_4$ solution (Fig.2.2).
Unfortunately there are no data for the system Na-SO_4-ClO_4, but the TcO_4^- ion has properties very similar to those of the ClO_4^- ion. The Pitzer parameters in the systems
Na-SO_4-Cl [a)] and Na-SO_4-TcO_4 [b)] are very well known and ascertained by numerous isopiestic and solubility data. The results are shown on the next page. They show that the corresponding differences in the trace activity coefficients of CO_3^{2-} and SO_4^{2-} are comparable, not only qualitatively but also quantitatively.

[a)] Harvie, Møller, Weare, Geochim. Cosmochim. Acta. 48 (1984), 723

[b)] Neck, Könnecke, Fanghänel, Kim, J. Solution Chem. 27 (1998), 107 and
Neck, Könnecke, Fanghänel, Kim, Radiochim. Acta 83 (1998), 75.

2) Trace activity coefficients of the H^+ ion in NaCl and CsCl solution.
The values shown in Fig.2.3 are calculated with the Pitzer parameters in [91PIT] evaluated from the experimental emf data.

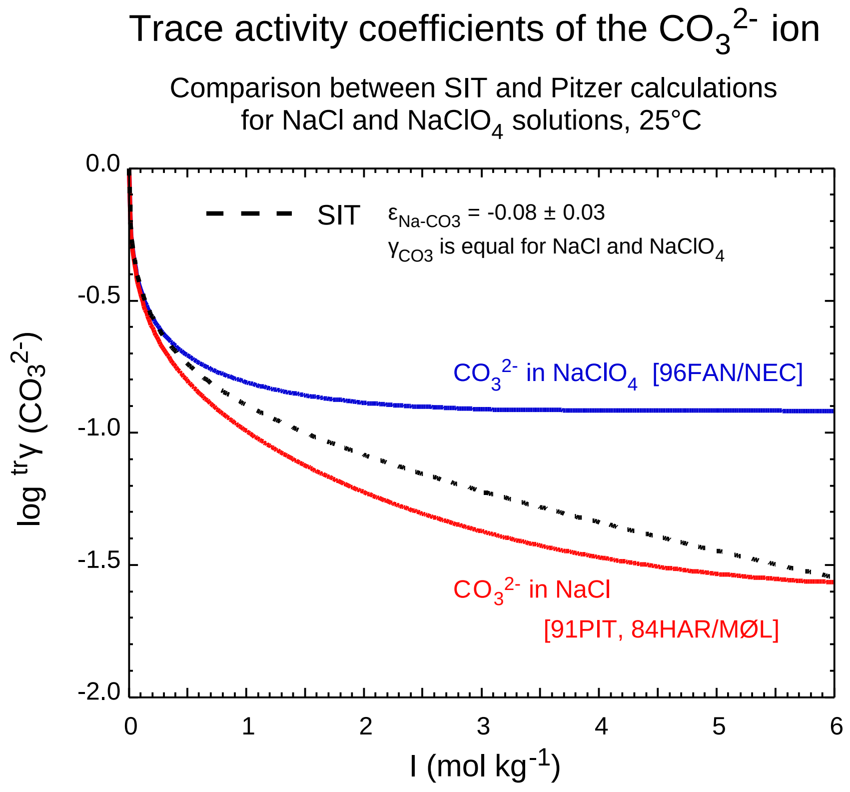

Trace activity coefficients of the CO_3^{2-} ion
Comparison between SIT and Pitzer calculations
for NaCl and $NaClO_4$ solutions, 25°C
SIT
ε_{Na-CO3} = -0.08 ± 0.03
γ_{CO3} is equal for NaCl and $NaClO_4$
CO_3^{2-} in $NaClO_4$ [96FAN/NEC]
CO_3^{2-} in NaCl
[91PIT, 84HAR/MØL]
log $^{tr}\gamma$ (CO_3^{2-})
0.0
-0.5
-1.0
-1.5
-2.0
0
1
2
3
4
5
6
I (mol kg^{-1})

Fig. 2.1

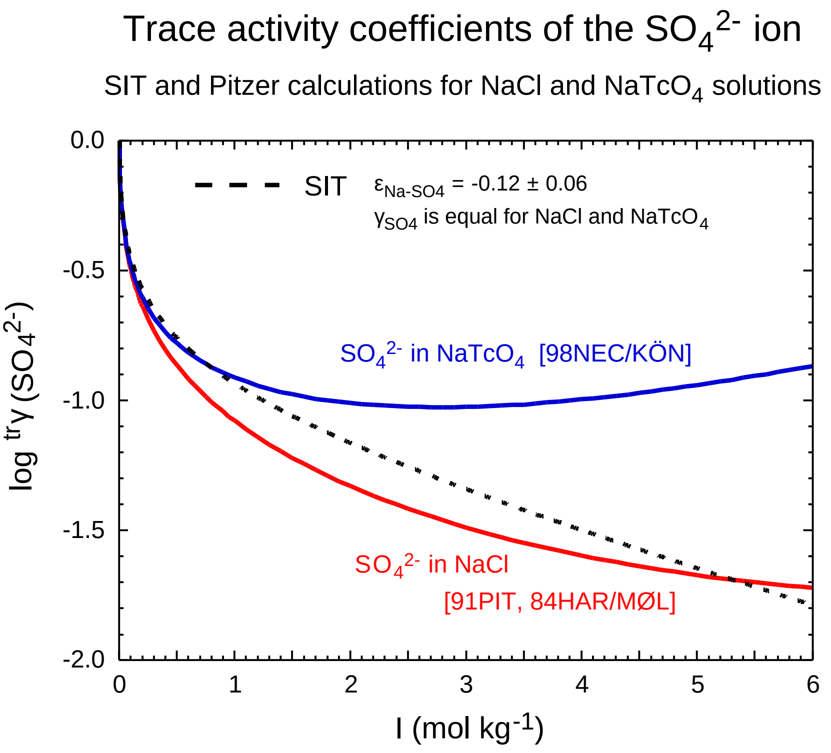

Trace activity coefficients of the SO_4^{2-} ion
SIT and Pitzer calculations for NaCl and $NaTcO_4$ solutions
SIT
ε_{Na-SO4} = -0.12 ± 0.06
γ_{SO4} is equal for NaCl and $NaTcO_4$
SO_4^{2-} in $NaTcO_4$ [98NEC/KÖN]
SO_4^{2-} in NaCl
[91PIT, 84HAR/MØL]
log $^{tr}\gamma$ (SO_4^{2-})
0.0
-0.5
-1.0
-1.5
-2.0
0
1
2
3
4
5
6
I (mol kg^{-1})

Fig. 2.2

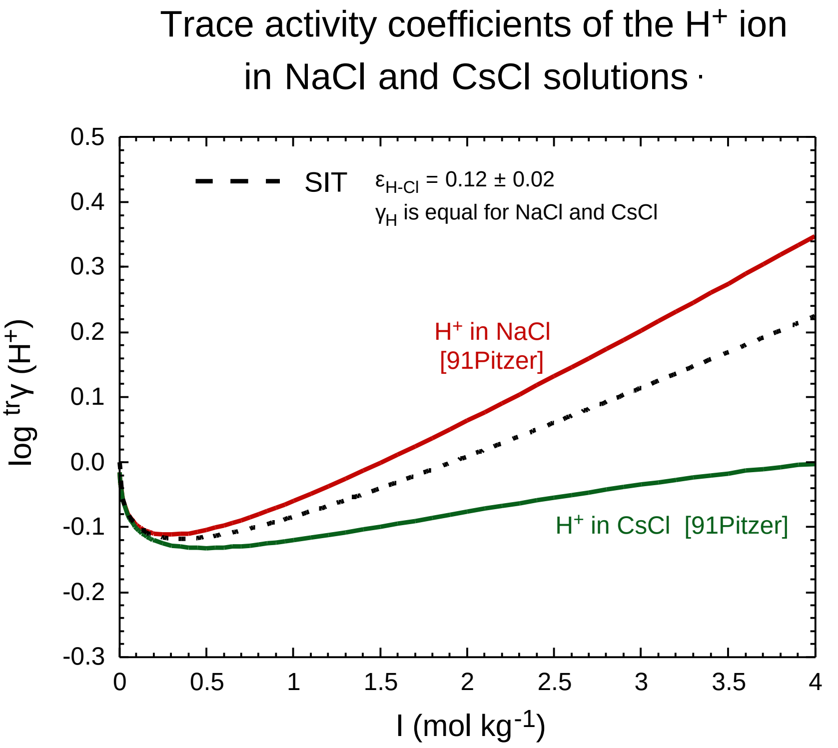

Trace activity coefficients of the H+ ion in NaCl and CsCl solutions
SIT
εH-Cl = 0.12 ± 0.02
γH is equal for NaCl and CsCl
H+ in NaCl [91Pitzer]
H+ in CsCl [91Pitzer]
log trγ (H+)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
0
0.5
1
1.5
2
2.5
3
3.5
4
I (mol kg-1)

Fig. 2.3

2.2. Actinide carbonate solids of Np(V), Am(III), U(VI); consequences for solubility constants at I = 0

$NaNpO_2CO_3(s)$, $Na_3NpO_2(CO_3)_2(s)$, $Am_2(CO_3)_3(s)$, $UO_2CO_3(s)$

Since the carbonate trace activity coefficient is directly involved in the solubility constants for actinide carbonate solid phases (and of course also in the formation constants of aqueous carbonte complexes) at I = 0, the consequences of the different set of auxiliary data is shown in the following sections. Because of the limited time, the present calculations are restricted to the solid phases $NaNpO_2CO_3(s)$, $Na_3NpO_2(CO_3)_2(s)$, $Am_2(CO_3)_3(s)$ and $UO_2CO_3(s)$

Neptunium(V)

Solubility constant for $NaNpO_2CO_3{\cdot}xH_2O(s)$

In the NEA review, the results of Kim and coworkers [91KIM/KLE, 94NEC/RUN, 94NEC/KIM, 94RUN/KIM, 95NEC/RUN, 95NEC/FAN, 95FAN/NEC] as well as those of former coworkers of this group [94MEI, 96RUN/NEU] were generally critisized to be not reliable and disregarded (open points in Fig.2.4). Particularly in the case of the data in NaCl solution and in 0.1 M $NaClO_4$, this is a pure arbitrary act of the reviewer, since all auxiliary data used in these studies (ion product of water, H_2CO_3 dissociation constants) are consistent with the NEA-TDB.

The evaluation of the solubility constant at I = 0 is primarily based on solubility studies of Maya [83MAY] (in 1 M $NaClO_4$) and Vitorge (in 3 M $NaClO_4$) reported in [86GRE/ROB] and later again in [90RIG]. Further, the reviewer applied the SIT coefficients from the NEA-TDB ($\varepsilon(Na^+/ClO_4^-) = 0.01$, $\varepsilon(Na^+/CO_3^{2-}) = -0.08$ and $\varepsilon(NpO_2^+/ClO_4^-) = 0.25$ [85SIL/BID]), and hence $\Delta\varepsilon = 0.18$) to calculate the constants at I = 0.
As a consequence, the reviewer concludes that the results of Maya [83MAY] refer to a hydrated solid phase and those of Vitorge [86GRE/ROB] to an aged, less hydrated solid phase with

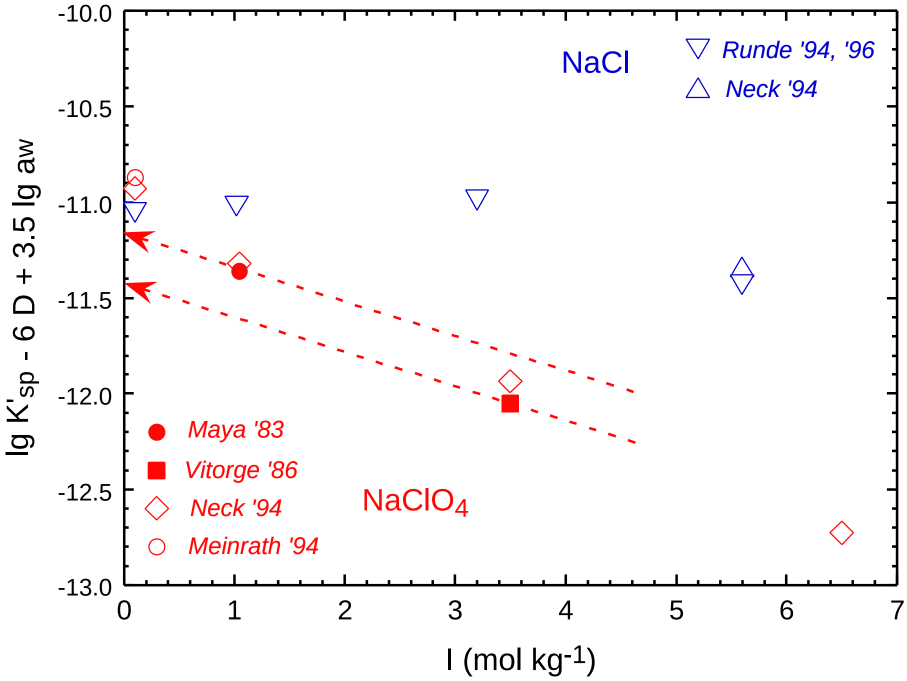
$\log K°_s = -11.16 \pm 0.35$ for $NaNpO_2CO_3{\cdot}3.5H_2O(s)$

and

$\log K°_s = -11.66 \pm 0.50$ for $NaNpO_2CO_3(s)$, aged

NEA review (VITORGE)

Solubility product of $NaNpO_2CO_3 \cdot x\ H_2O$ (x = 3.5 and x = 0)



Vitorge: 1) Data of Kim's group (open points) are not considered !

2) SIT coefficients are taken from the NEA-TDB

- - - - NEA-TDB:
$\Delta\varepsilon = 0.18 \pm 0.06$

NpO_2^+ / ClO_4^- $\varepsilon = 0.25$
Na^+ / ClO_4^- $\varepsilon = 0.01$
Na^+ / CO_3^{2-} $\varepsilon = -0.08$

Fig. 2.4

In Fig.2.4, the original log K_s value given in [86GRE/ROB, 90RIG] is used to extrapolate Vitorge's data in 3.5 m $NaClO_4$ to I = 0. In the NEA review a lower value is evaluated (c.f. discussion of [90RIG], p.795-798, Appendix A). However, this recalculation is somewhat speculative. It is based on the assumptions that the scattering of the experimental data is due to the presence of different solid phases and that the lowest solubility data refer to aged $NaNpO_2CO_3$(s).

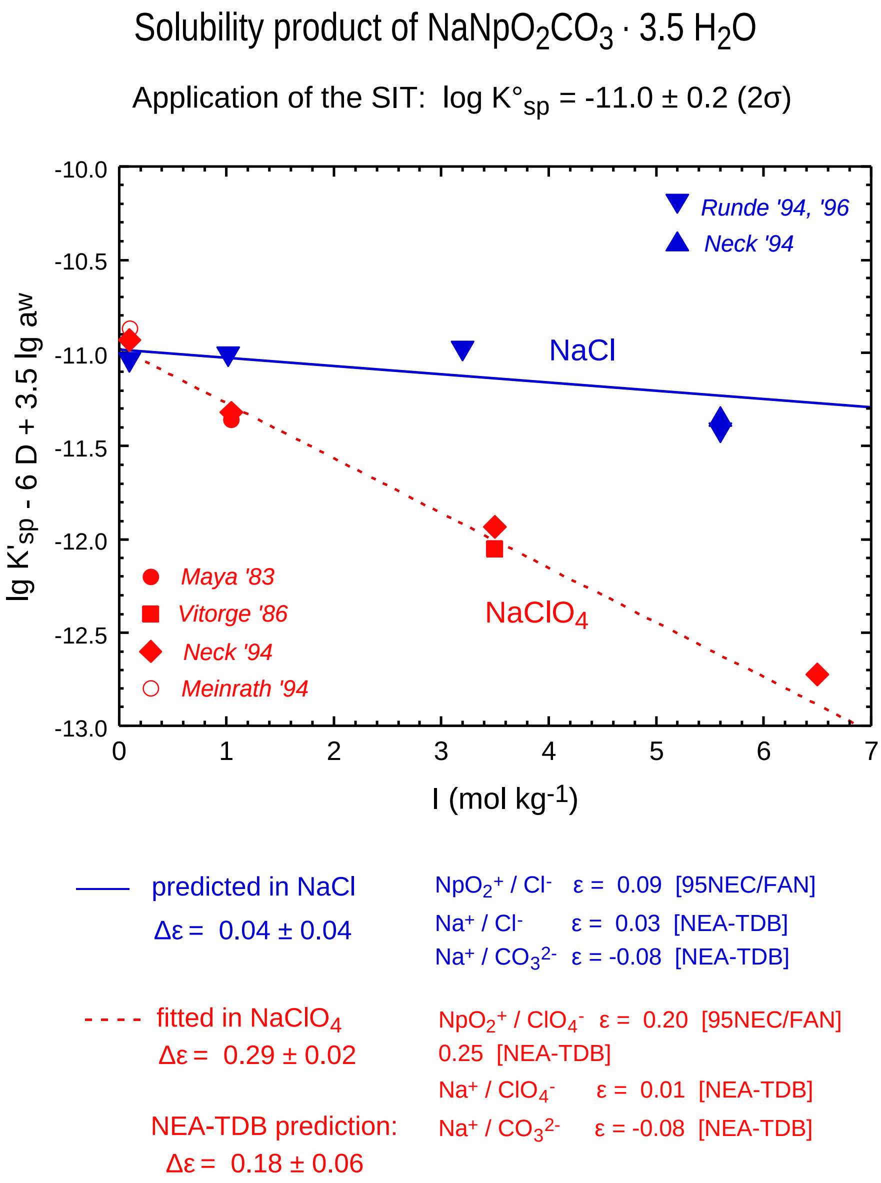


Fig. 2.5

Fig. 2.5 shows the SIT extrapolation to I = 0, including as well the results of Kim and coworkers. It is to note that the solid line (for the data in NaCl solution) is predicted by independent SIT coefficients: $\varepsilon(Na^+/Cl^-) = 0.03$ and $\varepsilon(Na^+/CO_3^{2-}) = -0.08$ from the NEA-TDB [85SIL/BID], $\varepsilon(NpO_2^+/Cl^-) = 0.09$ from a solvent extraction study in [95NEC/FAN], and hence $\Delta\varepsilon = 0.04$. For both media (NaCl and $NaClO_4$) the extrapolation to I = 0 leads to a consistent value of $\log K°_s = -11.0 \pm 0.2$.

As already documented in section 1.1 of this manuscript, the solubility data in [91KIM/KLE, 94NEC/RUN, 94NEC/KIM, 94RUN/KIM, 95NEC/RUN, 95NEC/FAN, 95FAN/NEC, 96RUN/NEU] refer to the same solid phase, the hydrated $NaNpO_2CO_3 \cdot 3.5H_2O(s)$ described by Volkov et al. [77VOL/VIS] and Maya [83MAY]. (Solely Meinrath [94MEI] reported an other

(hexagonal) modification of $NaNpO_2CO_3 \cdot xH_2O(s)$, with different x-ray pattern).
However, as expected according to section 1.2, the value of $\Delta\varepsilon = 0.29$ in $NaClO_4$ solution (dashed line) deviates significantly from the NEA-TDB prediction, because the value of $\varepsilon(Na^+/CO_3^{2-}) = -0.08$ is appropriate for the carbonate trace activity coefficients in NaCl, but not for those in $NaClO_4$ solution (c.f. discussion in 2.1). The dashed line would be predicted with $\varepsilon(Na^+/CO_3^{2-}) = +0.04$ (in $NaClO_4$ solution), evaluated in section 2.3 from the H_2CO_3 dissociation constants determined in [96NEC/FAN].

In the table below (next page) auxiliary data given in the NEA-TDB for $\varepsilon(Na^+/Cl^-)$, $\varepsilon(Na^+/ClO_4^-)$ and $\varepsilon(Na^+/CO_3^{2-})$, together with $\varepsilon(NpO_2^+/Cl^-) = 0.09$ and $\varepsilon(NpO_2^+/ClO_4^-) = 0.20$ are used to calculate the solubility product of $NaNpO_2CO_3 \cdot xH_2O(s)$ at I = 0. It becomes evident that (within the range of experimental uncertainties) all studies in NaCl solution lead to a consistent value of log K°_s, in particular if we assume the hydration number of x = 3.5 given in [83MAY].

In the same table, analogous calculations are done with the data published in $NaClO_4$ solution. Again the auxiliary interaction coefficients from the NEA-TDB are used (with the exception that $\varepsilon(NpO_2^+/ClO_4^-) = 0.20$ 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 in NaCl solution, the calculated log K°_s values are not consistent. They decrease systematically with increasing $NaClO_4$ concentration.
Remember: $\varepsilon(Na^+/CO_3^{2-}) = -0.08$, the SIT coefficient of the NEA-TDB was not appropriate for the carbonate trace activity coefficients in $NaClO_4$ solution above 1 molal (Fig. 2.1).

In the next table, we use the Pitzer parameters for the carbonate ion (from [91PIT, 96FAN/NEC] and for the NpO_2^+ ion from [95NEC/FAN] to calculate log K°_s.
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 M in both, NaCl and $NaClO_4$ solutions). The average value is found to be

$$\log K^\circ_s = -11.08 \pm 0.20 \ (2\sigma) \quad \text{for } NaNpO_2CO_3 \cdot 3.5H_2O(s)$$

It is to note that the SIT or Pitzer coefficients for the NpO_2^+ ion are based on the same experimental input data. That means: the only essential difference between SIT and Pitzer calculations is that for γCO_3^{2-} !
The consistency of the values calculated for I = 0 may be considered as a corroboration of the activity coefficients used, which justifies the SIT extrapolation in Fig.2.5.

Solubility products of hydrated $NaNpO_2CO_3 \cdot xH_2O(s)$ at 20 - 25°C
SIT calculation with auxiliary data from the NEA-TDB

Ref.	Medium	log K_s	log K°_s (I = 0) a)	
		(molar)	x = 0	x = 3.5

a) in 0.1 - 5 M NaCl

[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) [b)]
[94NEC/KIM]	5.0 M NaCl	- 9.52	(-10.74	-11.12) [b)]

b) in 0.1 - 5 M NaClO$_4$

[91KIM/KLE, 94NEC/RUN]	0.1 M NaClO$_4$	-10.28	-10.92	-10.92
[94MEI]	0.1 M NaClO$_4$	-10.22	-10.86	-10.86
[83MAY]	1.0 M NaClO$_4$	-10.14	-11.18	-11.23
[91KIM/KLE, 94NEC/RUN]	1.0 M NaClO$_4$	-10.10	-11.14	-11.19
[86GRE/ROB]	3.0 M NaClO$_4$	-10.56	-11.41	-11.60
[91KIM/KLE, 94NEC/RUN]	3.0 M NaClO$_4$	-10.45	-11.30	-11.49
[94NEC/RUN]	5.0 M NaClO$_4$	-11.06	(-11.49	-11.87) [b)]

[a)] NEA-TDB [95SIL/BID]: ε(Na^+/ClO_4^-) = 0.01, ε(Na^+/Cl^-) = 0.03, ε(Na^+/CO_3^{2-}) = -0.08 ε(NpO_2^+/ClO_4^-) = 0.20, and ε(NpO_2^+/Cl^-) = 0.09

[b)] at this concentration the SIT may become inaccurate

Solubility products of hydrated $NaNpO_2CO_3 \cdot xH_2O(s)$ at 20 - 25°C

Pitzer calculation (Fanghänel, Neck)

Ref.	Medium	log K_s (molar)	log $K°_s$ (I = 0) 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
[91KIM/KLE, 94NEC/RUN]	0.1 M $NaClO_4$	-10.28	-10.94
[94MEI]	0.1 M $NaClO_4$	-10.22	-10.88
[83MAY]	1.0 M $NaClO_4$	-10.14	-11.18
[91KIM/KLE, 94NEC/RUN]	1.0 M $NaClO_4$	-10.10	-11.14
[86GRE/ROB]	3.0 M $NaClO_4$	-10.56	-11.25
[91KIM/KLE, 94NEC/RUN]	3.0 M $NaClO_4$	-10.45	-11.14
[94NEC/RUN]	5.0 M $NaClO_4$	-11.06	-11.08

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

Solubility constant for $Na_3NpO_2(CO_3)_2(s)$

In the table below, the experimental solubility constants reported for $Na_3NpO_2(CO_3)_2(s)$ in 1, 3 and 5 M $NaClO_4$ and in 5 M NaCl [86GRE/ROB, 91KIM/KLE, 94RUN/KIM, 95NEC/RUN] are extrapolated to I = 0. The results are comparable with those observed for $NaNpO_2CO_3 \cdot xH_2O(s)$. If SIT coefficients are used, with γCO_3^{2-} according to the NEA-TDB, the calculated log $K°_s$ values decrease systematically with increasing $NaClO_4$ concentration, whereas the Pitzer parameters given in [95NEC/FAN, 96FAN/NEC] lead to consistent values of log $K°_s$.

Again it is to note that the SIT or Pitzer coefficients for the NpO_2^+ ion are based on the same experimental input data. That means: the only essential difference between SIT and Pitzer calculations is that for γCO_3^{2-} !!!

Solubility product of $Na_3NpO_2(CO_3)_2(s)$ at 20 - 25°C

Ref.	Medium	log K_s (molar)	log $K°_s$ (I = 0) SIT a)	Pitzer c)
[94NEC/RUN]	1.0 M $NaClO_4$	-12.23	-14.5	-14.5
[86GRE/ROB]	3.0 M $NaClO_4$	-12.44	-14.8	-14.2
[94NEC/RUN]	3.0 M $NaClO_4$	-12.59	-14.9	-14.4
[94NEC/RUN]	5.0 M $NaClO_4$	-13.57	(-15.7) b)	-14.3
[94RUN/KIM] [95NEC/RUN]	5.0 M NaCl	-11.46	(-14.2) b)	-14.2

a) NEA-TDB [95SIL/BID]: $\varepsilon(Na^+/ClO_4^-) = 0.01$, $\varepsilon(Na^+/Cl^-) = 0.03$, $\varepsilon(Na^+/CO_3^{2-}) = -0.08$
$\varepsilon(NpO_2^+/ClO_4^-) = 0.20$, and $\varepsilon(NpO_2^+/Cl^-) = 0.09$

b) at this concentration the SIT may become inaccurate

c) calculated with Pitzer parameters given in [95NEC/FAN, 96FAN/NEC]

Note: The only essential difference between SIT and Pitzer calculations is that for γCO_3^{2-} !!!

Americium(III)

For the hydrated $Am_2(CO_3)_3 \cdot xH_2O(s)$ there are experimental results from Meinrath and Runde (Kim's research group) in 0.1 M $NaClO_4$ and from Robouch (Vitorge's research group) in 3.0 M $NaClO_4$. These data were extrapolated to I = 0 in the NEA review [95SIL/BID], and the resulting values were found to be strongly inconsistent. Since it is not clear whether more or less crystalline solid phases were obtained in these studies, the NEA review recommended an average value with a large uncertainty:

$\log K°_s = -16.7 \pm 1.1$ [95SIL/BID]

If we use the γCO_3^{2-} values from [96FAN/NEC] to calculate the equilibrium constants at I = 0, the consistency is considerably increased, and the mean value of the two research groups has a significantly smaller uncertainty:

$\log K°_s = -16.6 \pm 0.4$ (2σ)

Hydrated $Am_2(CO_3)_3 \cdot xH_2O(s)$ at 20 - 25°C;
Solubility constant log K_s for the reaction: $0.5\ Am_2(CO_3)_3(s) \Longleftrightarrow Am^{3+} + 1.5\ CO_3^{2-}$

Ref.	Medium	log K_s	log $K°_s$ (I = 0)	
		(molar)	SIT NEA-TDB [a]	γCO_3^{2-} from [96FAN/NEC] [b]
[92RUN/MEI]	0.1 M $NaClO_4$	- 14.73	- 16.33	- 16.3
[91MEI/KIM]	0.1 M $NaClO_4$	- 14.90	- 16.50	- 16.5
[91MEI/KIM2]	0.1 M $NaClO_4$	- 14.79	- 16.39	- 16.4
[89ROB]	3.0 M $NaClO_4$	- 15.08 (-15.27) [c]	- 17.36 (-17.54) [c]	- 16.8

[a] calculated with $\varepsilon(Am^{3+}/ClO_4^-) = 0.49$ and $\varepsilon(Na^+/CO_3^{2-}) = -0.08$ [95SIL/BID], for x = 0

[b] γAm^{3+} is the same as in a), whereas γCO_3^{2-} is taken from [96FAN/NEC]

[c] recalculated in [95SIL/BID]. The original values in [89ROB] are corrected by using a somewhat different H_2CO_3 dissociation constant to calculate log $[CO_3^{2-}]$ from log [H+]. However, since the calibration of Robouch is internally consistent, such a recalculation does not "correct" the data of Robouch. It makes them incorrect.

Uranium(VI)

In the case of the solubility product of UO_2CO_3(s) at 20 -25°C, the experimental data published before 1992 are discussed and extrapolated to I = 0 in the previous NEA review [92GRE/FUG]. In the literature published later, there are numerous studies in 0.1 M $NaClO_4$, which can be devided into two groups. One set of results leads to log $K°_s$ = -14.2 ± 0.2, which is in the range of the previous results discussed in [92GRE/FUG]. The other set of results, from laboratories in Japan (Meinrath, Kimura, Kato) lead to a significant lower solubility constant of log $K°_s$ = -14.9 ± 0.2.

Independent of the auxiliary data used to calculate γCO_3^{2-} in $NaClO_4$ solution (either SIT coefficients from [95SIL/BID] or Pitzer parameters from [96FAN/NEC]), the calculated values of log $K°_s$ are ranging from -14.1 to -14.5, or even to -14.9 ± 0.2 if we include the data from [93MEI/KIM, 93MEI/KIM2, 96MEI/KAT, 96KAT/KIM], respectively.

From the data reported in [72/SER/NIK, 76NIK2, 84GRE/FER, 92KRA/BIS, 93PAS/RUN, 96MEI/KLE], the following unweighted overall mean values (± 2σ) are obtained:

log $K°_s$ = -14.32 ± 0.30 (with γCO_3^{2-} according to [95SIL/BID])

or

log $K°_s$ = -14.27 ± 0.28 (with γCO_3^{2-} according to [96FAN/NEC])

The consistency obtained with γCO_3^{2-} according to [95SIL/BID] or according to [96FAN/NEC] is approximately the same.

Solubility product of $UO_2CO_3(s)$ at 20 -25°C

Ref.	Medium	log K_s (molar)	log $K°_s$ (I = 0)	
			SIT NEA-TDB [a)]	γCO_3^{2-} from [96FAN/NEC] [b)]
[92GRE/FUG] NEA-TDB review			-14.47 ± 0.04	
[72/SER/NIK]	I = 0.0002 - 0.02 M		-14.26 ± 0.3	-14.26 ± 0.3
[76NIK2]	I = 0.01 M	-14.15	-14.50	-14.50
[92KRA/BIS,]	0.1 M $NaClO_4$	-13.29	-14.11	-14.12
[93PAS/RUN]		-13.35	-14.18	-14.19
[96MEI/KLE]		-13.50	-14.33	-14.34
[84GRE/FER]	0.5 M $NaClO_4$	-13.21	-14.40	-14.37
[84GRE/FER]	3.0 M $NaClO_4$	-13.94	-14.48	-14.12
<u>New data</u>				
[92KRA/BIS]	0.1 M $NaClO_4$	-13.29	-14.11	
[93PAS/RUN]	”	-13.35	-14.18	
[96MEI/KLE]	”	-13.50	-14.33	
mean value (± 2σ)		-13.38 ± 0.22	-14.21 ± 0.22	-14.22 ± 0.22
[93MEI/KIM]	0.1 M $NaClO_4$	-13.89	-14.72	
[93MEI/KIM2]	”	-14.18	-15.01	
[96MEI/KAT]	”	-14.05	-14.88	
[96KAT/KIM]	”	-14.10	-14.93	
mean value (± 2σ)		-14.06 ± 0.24	-14.89 ± 0.24	-14.90 ± 0.24

[a)] calculated with $\varepsilon(UO_2^{2+}/ClO_4^-) = 0.46$ [92GRE/FUG], $\varepsilon(Na^+/CO_3^{2-}) = -0.08$ [95SIL/BID]

[b)] γUO_2^{2+} is the same as in a), whereas γCO_3^{2-} is taken from [96FAN/NEC]

2.3. Proposal to solve the problem of carbonate trace activity coefficients:

In the tables above, the solubility constants at I = 0 for actinide carbonate solids are partly based on SIT activity coefficients and partly on Pitzer activity coefficients. Such a mixing is certainly not desirable and not acceptable for the NEA-TDB. Therefore, it is necessary to find a solution, which is based exclusively on the SIT formalism.

1) At first, we have to recognize that interactions anion/anion and cation/cation are not generally negligible as experimentally demonstrated (c.f. examples H^+ in NaCl / H^+ in CsCl and SO_4^{2-} in NaCl / SO_4^{2-} in $NaTcO_4$; Figs. 2.1 - 2.3.). If we consider <u>traces of cation C or anion A in an electrolyte solution MX</u>, the values of "ε(C/X)" and "ε(A/M)" actually represent the sums:

$$“\varepsilon(C/X)“ = \varepsilon(C/X) + \varepsilon(C/M)$$

and

$$“\varepsilon(A/M)“ = \varepsilon(A/M) + \varepsilon(A/X)$$

2) In the original SIT equation neither these anion/anion and cation/cation interactions nor interaction between neutral solutes and ions are explicitely excluded. Setting ε(C/M) and ε(A/X) equal to zero is an (over)simplification, which fairly works in many cases. E.g. in the case of OH^- trace activity coefficients in NaCl and $NaClO_4$ solution. Therefore, fortunately, we do not have problems to describe the ion product of water or solubility constants for actinide hydroxides with the same value of "$\varepsilon(OH^-/Na^+)$". However, anion/anion interactions generally become important if the charge of an anion is -2 or larger, e.g. for SO_4^{2-}, CO_3^{2-} and the Np(V) carbonate complexes $NpO_2(CO_3)_n^{1-2n}$.

In order to avoid the explicite evaluation of ε values for anion/anion and cation/cation interactions, we could indicate that "ε(C/X)" and "ε(A/M)" values are valid for the medium MX by introducing the definitions:

$$\varepsilon(C/X)_{MX} = \varepsilon(C/X) + \varepsilon(C/M)$$
$$\varepsilon(A/M)_{MX} = \varepsilon(A/M) + \varepsilon(A/X)$$

3) It is to note that in [80CIA] and the NEA-TDB, there are many SIT coefficients derived from binary system osmotic coefficients. In these cases, they actually represent ε(C/A) values. We neglect cation/cation interactions ε(C/M) and use ε(C/A) as $\varepsilon(C/A)_{MA}$ to calculate trace activity coefficients of C in the medium MA (e.g. for C = UO_2^{2+}, Nd^{3+} as analog for Am^{3+}, and MA = NaCl or $NaClO_4$). If the medium cation is always M = Na^+, we will probably not run into trouble, but we have to take care with data in other media, e.g. $MgCl_2$.

Trace activity coefficients of the carbonate ion in NaCl solution

In 0 - 3 M NaCl solution, the SIT coefficient proposed in the NEA-TDB:

$\varepsilon(Na^+/CO_3^{2-})_{NaCl} = \varepsilon(Na^+/CO_3^{2-}) + \varepsilon(Cl^-/CO_3^{2-}) = \underline{-(0.08 \pm 0.03)}$ [95SIL/BID]

accurately describes the experimental data for the equilibria

$NaNpO_2CO_3 \cdot 3.5H_2O(s) \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{2-} + 3.5\,H_2O$

and

$CO_2(g) + H_2O \Leftrightarrow 2\,H^+ + CO_3^{2-}$

In Fig.2.1, there are certain differences, if $\gamma(CO_3^{2-})$ is calculated with this SIT coefficient or the known Pitzer parameters. The Pitzer activity coefficients would be better described with a SIT coefficient of $\varepsilon(Na^+/CO_3^{2-})_{NaCl} = -0.11$. These discrepancies are probably due to different exp. input data. (To a certain extent they might also be due to small differences in the splitting conventions because of the triple ion interactions or higher order terms in the Pitzer equations). However combined with the differences in $\gamma(H^+)$ they cancel out for the equilibrium $CO_2(g) + H_2O \Leftrightarrow 2\,H^+ + CO_3^{2-}$. For reasons of consistency the value of $\varepsilon(Na^+/CO_3^{2-})_{NaCl} = -(0.08 \pm 0.03)$ given in the NEA-TDB [95SIL/BID] should not be changed.

Trace activity coefficients of the carbonate ion in NaClO$_4$ solution

$\varepsilon(Na^+/CO_3^{2-})_{NaClO4} = \varepsilon(Na^+/CO_3^{2-}) + \varepsilon(ClO_4^-/CO_3^{2-})$

For the two equilibria given above there are sufficient experimental data to determine the activity and SIT coefficients of the carbonate ion in NaClO$_4$ solution:

(1) $NaNpO_2CO_3 \cdot 3.5H_2O(s) \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{2-} + 3.5\,H_2O$

Fig. 2.5: SIT plot with exp. data from [83MAY, 86GRE/ROB, 94NEC/RUN, 94MEI] This includes the assumption that the reported solubility data refer to the same solid phase. For the data from [83MAY, 94NEC/RUN] this is well ascertained.

$\Rightarrow \log K° = -11.0 \pm 0.2$; $(\Delta\varepsilon)_{NaClO4} = 0.29 \pm 0.02$

$$\begin{aligned}\varepsilon(Na^+/CO_3^{2-})_{NaClO4} &= (\Delta\varepsilon)_{NaClO4} - \varepsilon(Na^+/ClO_4^-) - \varepsilon(NpO_2^+/ClO_4^-)\\ &= (0.29 \pm 0.02) - (0.01 \pm 0.01) - (0.22 \pm 0.03)^* = \underline{+(0.06 \pm 0.04)}\end{aligned}$$

* mean value of $\varepsilon(NpO_2^+/ClO_4^-) = 0.25 \pm 0.05$ (NEA-TDB, from redox measurements of Vitorge et al.) and 0.20 ± 0.03 (from solvent extraction study in [95NEC/FAN])

(2) $CO_2(g) + H_2O \Leftrightarrow 2\,H^+ + CO_3^{2-}$

Fig. 2.6: SIT plot with exp. data from [96FAN/NEC]; log K° fixed from NEA-TDB

$$\begin{aligned}\varepsilon(Na^+/CO_3^{2-})_{NaClO4} &= (\Delta\varepsilon)_{NaClO4} - 2\,\varepsilon(H^+/ClO_4^-)\\ &= (0.32 \pm 0.03) - 2\cdot(0.14 \pm 0.02) = \underline{+(0.04 \pm 0.05)}\end{aligned}$$

The values derived from equilibria (1) and (2) are consistent and a mean value of $\varepsilon(Na^+/CO_3^{2-})_{NaClO4}$ = +(0.05 ± 0.05) could be proposed.

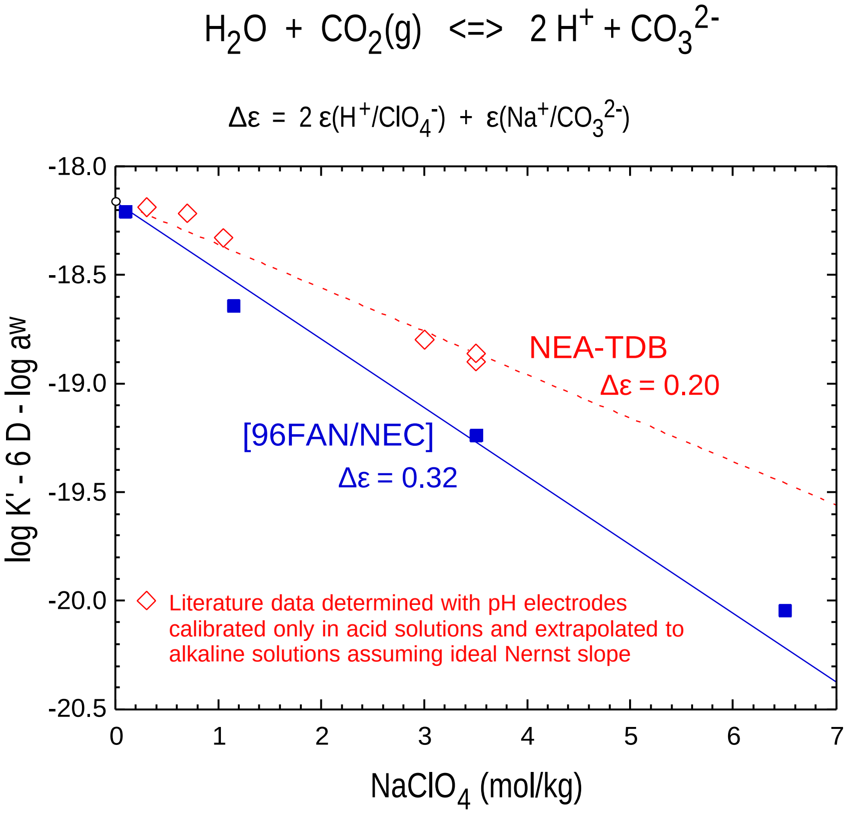


Fig. 2.6

Another possibility to overcome the problem of different SIT coefficients in different media would be to calculate only Δε values for the reactions, which are then different for $NaClO_4$ and NaCl solution: $(\Delta\varepsilon)_{NaClO4}$. ≠ $(\Delta\varepsilon)_{NaCl}$.

2.4. Consequences for NEA-TDB reviews

(1) Limitations of the SIT have to be pointed out.

(2) The SIT has to be extended for anion-anion interactions (c.f. proposal), at least in cases where this is necessary to avoid erroneous conclusions

(3) a) New (correct) trace actvity coefficients for CO_3^{2-} in $NaClO_4$ should be used.

=> All ε coefficients of actinide carbonate complexes, derived from exp. data at high $NaClO_4$ concentrations should be reevaluated. The existing Δε values are of course not affected

If possible, the experimental results on H_2CO_3 dissociation constants given in [96FAN/NEC] should be checked in an independent laboratory.

b) As long as there is no final decision on the problem in 3a), only unambiguous data (in NaCl solution or at low $NaClO_4$ concentration, where the NEA-TDB auxiliary data on the carbonate ion are free of any doubt) should be used to evaluate SIT coefficients and equilibrium constants at $I = 0$.

c) Similar problems as in the case of trace actvity coefficients for CO_3^{2-} in $NaClO_4$ solution have to be expected for the SO_4^{2-} ion.

(4) Np/Pu review

a) Conclusions for solid Np(V) carbonates are incorrect. The selected log $K°_s$ values have to be changed.

b) log β°, and SIT parameters (Δε and ε) have to be reevaluated, including data in NaCl solution for the equilibria $NpO_2^+ + n\, CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_n^{1-2n}$ (or for the stepwise constants), because NaCl is an important medium with respect to natural aquatic systems. If necessary, the log β° values can be fixed from the corresponding extrapolation with data in $NaClO_4$ solution (c.f. Fig.2.7, next page). The known values of $\varepsilon(NpO_2^+/Cl^-)_{NaCl} = 0.09 \pm 0.02$ [95NEC/FAN] and $\varepsilon(Na^+/CO_3^{2-})_{NaCl} = -(0.08 \pm 0.03)$ can then be used to evaluate SIT coefficients $\varepsilon(Na^+/NpO_2(CO_3)_n^{1-2n})_{NaCl}$ for the Np(V) carbonate complexes in NaCl solution.

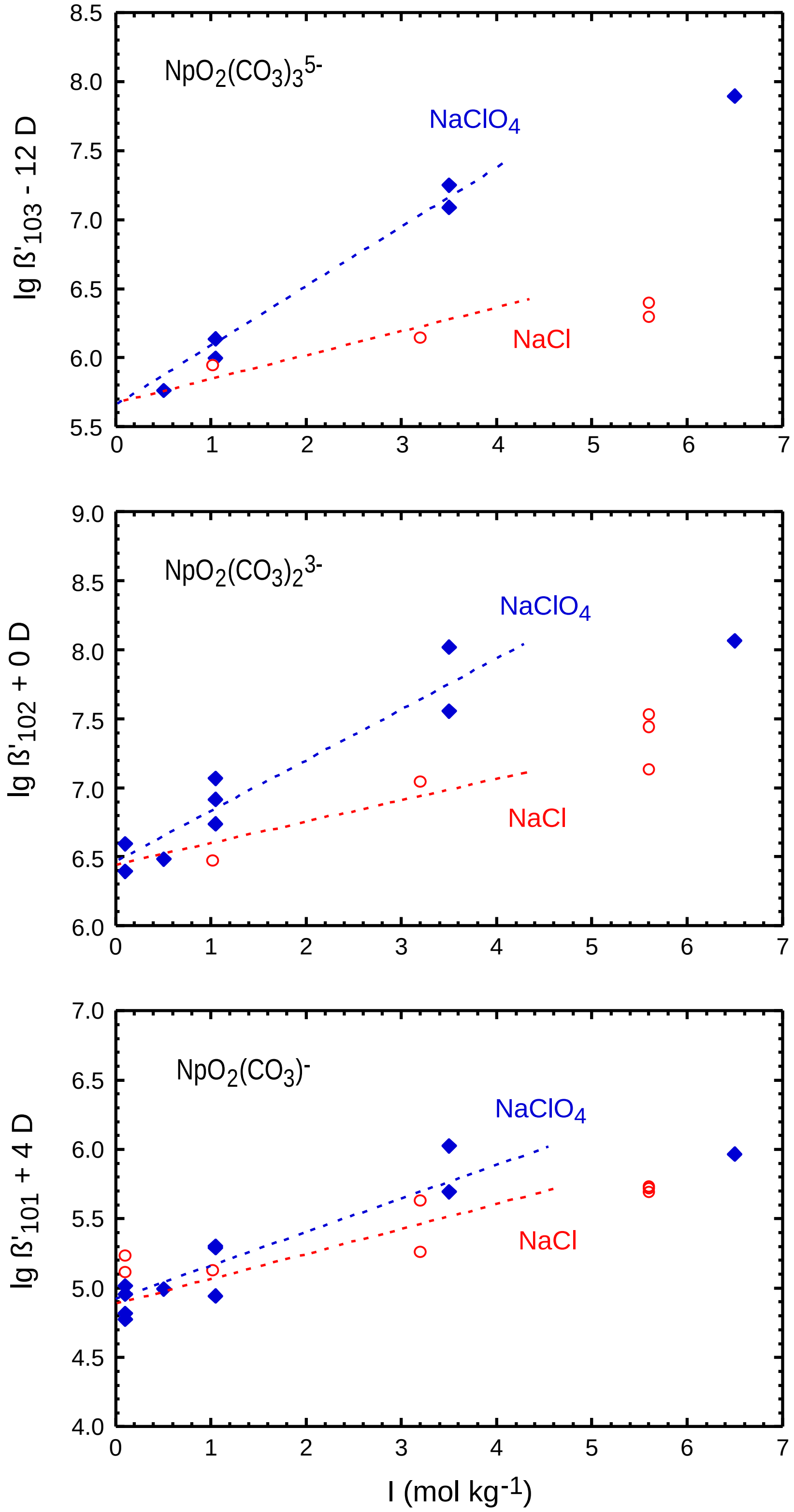

NpO2(CO3)3 5-
NaClO4
NaCl
lg ß'103 - 12 D
8.5
8.0
7.5
7.0
6.5
6.0
5.5
0
1
2
3
4
5
6
7
NpO2(CO3)2 3-
NaClO4
NaCl
lg ß'102 + 0 D
9.0
8.5
8.0
7.5
7.0
6.5
6.0
NpO2(CO3)-
NaClO4
NaCl
lg ß'101 + 4 D
7.0
6.5
6.0
5.5
5.0
4.5
4.0
I (mol kg-1)

Fig. 2.7

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4. Appendix

(Only available as hardcopy)

Appendix 1:	Schematic illustration of the titration vessels used in the solubility experiments of Neck and Runde
Appendix 2:	X-ray diffraction pattern from [94RUN/KIM]
Appendix 3:	Experimental solubility data in 0.1, 1 and 3 M $NaClO_4$ tabulated in the sequence of the measurements (Tables from [91KIM/KLE])
Appendix 4:	LSC spectra of Np-237 and daughter nuclide Pa-233