I have made remarks page by page on your last 44 page comments. It appears the main problem was wording in our draft. Your last comments do not really bring new qualitative or important information, but rather more details on what you previously wrote, hence the needed changes had been performed in the draft. As already said you proposed several interpretations that could be interesting; but for which more experimental confirmation are needed, hence our review did not rely on them. This mainly resulted in non considering your activity coefficients, which is quite a minor problem since for the system under discussion (Np(V) carbonate solubility product) the main goal of our review is to provide stoichiometries and equilibrium constants. The main subjects I commented are the following:

1. Despite what you wrote and repeated, we did not disregard you work. We even used data from your laboratory to select equilibrium constants and solubility product for all the components of the Np(V) carbonate system (this was already done before you started this polemic) with the same weight as similar works from other laboratories.

2. We originally found inconsistency between the values of NpO_2^+ activity coefficients extracted from your work using two different techniques (liquid-liquid extraction and solubility), hence on experimental data at high I. In the course of this discussion it appears that you propose to resolve this self inconsistency by adding a new term in the SIT formula used to calculate both CO_3^{2-} and NpO_2^+ activity coefficients. This results in a consistent interpretation of your data; but the values of NpO_2^+ activity coefficients extracted from your liquid-liquid extraction study are still poorly consistent with the corresponding value selected from the beginning of this series of reviews, a selection we confirmed. Anyhow I agree with you when you wrote (page 21 the paragraph before the last one) the main arises from experimental data and not in the choice of Pitzer versus SIT formula: it is first needed to confirm experimentally this problem with CO_3^{2-} activity coefficient: (i.e different value for pair parameter measured in NaCl and $NaClO_4$ media, while it should only depend on Na^+ concentration according to SIT hypothesis used in TDB review) at least because your interpretation is that most of the existing published data on this system in $NaClO_4$ aqueous solution would have systematic error, while your measurements would not. In other word the reverse explanation cannot be ruled out (see my comment page by page on your interpretation). It was actually the position of our review from the beginning (i.e before your starting this polemic): we recognised that auxiliary data used in our review (namely to calculate CO_3^{2-} activity coefficient) might need revision; but more experimental evidence is still needed. NpO_2^+ activity coefficients should not need revision at the moment (despite what you proposed which would) because emf measurements (on which the present value relies) are more reliable than solubility and liquid-liquid extraction techniques, and anyhow the new number you proposed is rather to fit inconsistency with one (yours) liquid-liquid extraction set of measurements. Anyhow these systematic deviations has no influence on the standard (i.e at I=0) values selected in our review, because we used a selection procedure that minimised this type of possible systematic error (whatever it is originated in your pH calibration or in TDB auxiliary value).

3. You also claimed that most published data in $NaClO_4$ media used wrong pH calibration (non nernstian slope of the glass electrode), you must be very sure of your own data to write this. You claimed this induced considerable difference in measured pH and hence in solubility product determinations that used this pH measurements. You said this difference could be of up to 0.2 unit log_{10} which is not so big and is in contradiction with what you wrote in a previous comments where you said that 0.2 unit log_{10} difference is not important in two of your determination of the first Np(V) carbonate complex constant using two different techniques (solubility and spectrophotometry: actually we agreed with your opinion, and we had written inconsistency was within your stated uncertainty that was certainly overoptimistic). So your supposed systematic error is within usual uncertainty. Actually it is even less for the solubility product under discussion: (following your reasoning) this 0.2 unit log_{10} is the maximum possible value at high pH, hence in chemical condition where Np(V) carbonate are formed, while the solubility product under discussion was fitted on data in more acidic (non complexing) media where the possible systematic deviation should be less. Typically in my own experimental determination from the number you provided (for the worst non nernstian glass electrode) I estimated the corresponding possible systematic deviation should be of 0.06 which is witin uncertainty (anyhow slope was independently checked in these measurements, and titration data were provided which allow a supplementary and they indeed confirmed the above estimatation).

4. For the solid phase under discussion, we found experimental evidence of ageing, but this information is not much reported in your publications because, as you wrote pages 6 you usually did not provide transient experimental measurement in the course of solubility measurement: you only reported the final, asymptotically reached equilibrium value (page 8) at equilibrium to deduce values for the equilibrium constants (we suspected it from the beginning). This is perfectly correct; but as a consequence we did not rely on your work to discuss solid phase ripening. You did not much discuss the published experimental evidence of solid phase transformation, nevertheless you claimed there is no problem with ageing of the solid. Statistical analysis of the standard values for those of published solubility products you provided, rather confirm our interpretation. You also calculated that it was possible to fit these published solubility products, this is neither completely convincing (for the above statistical reason and) because you added empirical terms and fitted parameters for activity coefficients in perchlorate media which are neither completely validated (above comment 2). In other words you might have seen evidence of interesting new phenomenon (typically anion-anion and triple interaction contribution to activity coefficient); but it cannot be ruled out that you simply added a new empirical term or a fitted parameter to compensate possible systematic error.

5. Instead of discussing published information on scattering of solubility data during the initial precipitation (in term of ageing: above comment 4) you claimed your solubility data are the most accurate among all the published ones, while (as recalled just here above) you wrote you eliminated from your reported data, the intermediary scattered ones. You used this artefact to claim (page 7) my results were not accurate. You also used similar trick to draw a figure in the same goal. No comment.
6. You proposed to add to the SIT formula, the above supplementary terms. This should be indeed useful if, as already said, your experimental observations are confirmed. To keep consistency with TDB, pair empirical parameters should keep the same values as in existing data set when possible, hence at least for a reference electrolyte. You typically used these extra terms in Pitzer formula for the $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ complexes while there is experimental evidence they are the same in chloride and perchlorate media, hence it should be possible to set them to zero in another most consistent (with existing SIT parameters) fitting exercise. Nevertheless, your treatment is mathematically perfectly correct. This does not seem possible for $NpO_2CO_3^-$ which can either be evidence of possible formation of a weak mixed complex, typically $NpO_2ClCO_3(aq)$.

I really considered all your arguments. Actually I completely rejected quite few of them: In most case I only asked for more experimental confirmations for the reasons explained or suggested in my page by page comments. I believe the (scientific) discussion is quite over:

Page 2
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.

PV 2a

Not generally, only on a specific minor problem in activity coefficient, generally our review found these works reliable enough to rely on in the selection of the standard complexation constants and solubility product. Only ionic strength corrections were not used. They were not used only on the following minor problem in activity coefficient calculations : possible inconsistency was found between the values of the interactions parameters $\varepsilon(NpO_2^+, ClO_4^-)$ calculated from your experimental studies using either solubility or liquid-liquid extraction techniques respectively, and anyhow inconsistency with TDB value. The origin of this inconsistency is still not resolved.

       This comment is certainly rather due to an impression, than to what was actually written in an anyhow draft version.

_____

the reviewer takes each opportunity to repeat the following reasons for disregarding the results of Kim and coworkers,

PV 2b

Yes, this was exaggerated and is now changed (see PV 2a concerning rewording)

_____

(a) chemical problems with the solid phase (insufficient knowledge on the equilibrium solid phase)

PV 2c

Problems in solid phase is discussed or suspected for all the published studies and supported by experimental results: x-ray diffraction patterns (see the figure) and kinetic observations. Your study is not used to discuss these problems, just because you only paid attention to obtain a stable reproducible solid phase, and not to discuss its ripening and evolution, hence you provided fewer information than in other studies : nothing is wrong with this. I still do not know whether you performed x-ray diffraction before solubility equilibration, or after (from your publications it rather seems it was characterisation of the phase initially used for solubility measurements).

       This comment is certainly rather due to an impression, than to what was actually written in an anyhow draft version : we did not criticised your solid phase.

_____

(b) systematic errors in pH calibration,

PV 2d

Not exactly, possible systematic error

       This comment is certainly rather due to an impression, than to what was actually written in an anyhow draft version, and anyhow rewording of the draft have now been performed to change this impression.

_____

(c) calculation of log [CO_3^{2-}] from measured log [H^+] with auxiliary data, which are inconsistent with the NEA-TDB

PV 2e

Where is the problem in this statement? You also wrote it

       This comment is certainly rather due to an impression, than to what was actually written in an anyhow draft version, and anyhow rewording of the draft have now been performed to change this impression (see also PV 2a).

_____

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).

PV 2f

The author of ref.[90RIG] is Riglet (Martial-Riglet) who is not a reviewer. She did her work in Vitorge's laboratory, who is a reviewer. The solubility work already appeared in ref. [86GRE/ROB] and is better documented in typically references [84VIT, 98VIT/CAP]. In references [84VIT, 86GRE/ROB, 98VIT/CAP] all measurements are reported including those which were a priori disregarded for chemical reasons (pH not stabilised, too short equilibration time, X-

ray analysis showing extra lines) prior to the treatment of the data, while they were not in Kim's et al. publications. Both presentation are correct; this was already said in our review, it has already been recognised in the course of the present discussion (PV 2f 5, 6e, 6c and 8a).
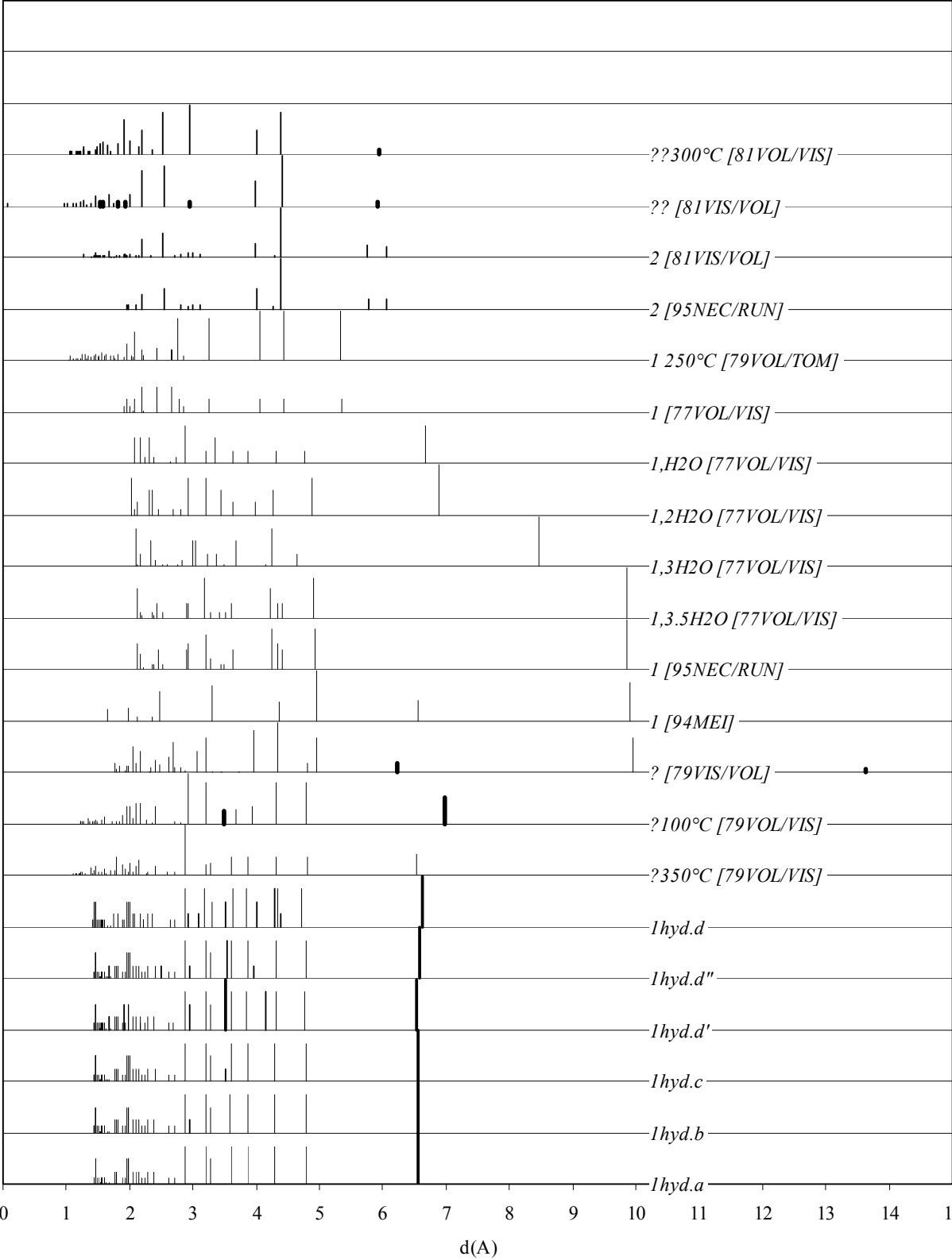
This comment is one of the aspect already discussed (see PV 2c): there are less experimental information and discussion on solid phase characterisation and evolution in your published solubility works, than in the studies used in our review to discuss solid phase formation.

_____

Statement (c) holds only for a part of our studies: for those in 1, 3 and 5 M NaClO₄,

PV 2g

Yes, there is an increasing systematic deviation with ionic strength, which is certainly within uncertainty for data at 0.1 M, (you did not published data in the range 0.1-1M, **n**evertheless, the systematic deviation should not be neglected in this range (I=0.1-1M)).

_____

 where the auxiliary data of the NEA-TDB are incorrect as will be shown in the present manuscript.

PV 2h

Yes, you pointed out, that you used data not much consistent with our auxiliary data, which resulted in different values for carbonic acid constants at high ionic strength, our review wrote (before receiving your comments) it might indicate our auxiliary data should be revised; but other possibilities are proposed to explain the deviation, typically possible liquid junction potential despite you measured it together with the influence of activity coefficients: it seems there are not enough redundant measurements for checking (making difference between liquid junction and activity coefficient effects), and anyhow, since this problem arose it might be better to check again the measurements using potentiometric cell of zero (or negligible) junction potential, and to compare with published data using such experimental set up. For these reasons, up to now our review did not adopt your values. Anyhow one cannot disregard, without further examination, the experimental values (some from famous old laboratories) used to established the TDB auxiliary values you criticise. The auxiliary values used in our review, are those adopted from the beginning (U review as already corrected in this particular case for $\varepsilon(Na^+, HCO_3^-)$ and $\varepsilon(Na^+, CO_3^{2-})$ as published in the Am book).

   Even if they are finally revised (and again this might be again necessary because they do not rely on enough and consistent experimental determinations in my opinion), this would anyhow not be enough to resolve the inconsistency found in our review in some activity coefficients for Np(V) (PV 2a and e).

_____

 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.

PV 2i

This means that published values for K in NaCl and $NaClO_4$ media are in poor agreement. In that case this should be first reviewed (again) and submitted to eventual future TDB specialists in charge of eventually changing these auxiliary values, possibly extra experimental measurement would be needed (see PV2 a, e and h).

   Your reasoning seems to be: (i) $\varepsilon(Na^+, HCO_3^-)$ and $\varepsilon(Na^+, CO_3^{2-})$ values used in our review reproduce K experimental values in NaCl, but not in $NaClO_4$ media; (ii) pair interaction parameters are not enough to model at least one of the two media (since $\varepsilon(H^+, ClO_4^-)$ and $\varepsilon(H^+, Cl^-)$ values are reliable). This is a possible physical explanation, but it is not clear why these extra parameters would be needed specifically for this (or these) system(s), and not on many other. Anyhow this discussion is on (ii), while we must first agree on experimental evidence on (i).

   It is now quite well established water dimer, trimer etc are formed in liquid water through (networks of) hydrogen bonds. Adding an ion locally modify it, and the first sphere hydration (water) molecules (of the added ion) can possibly be a starting points of co-operative hydrogen bonding, where (specially at high I) conterions could possibly participate to such network of (hydrogen bounds), this should result in ion pair which is usually taken into account at the macroscopic level by activity coefficients, specially in this particular case through second virial terms (ion pair empirical parameters). This could equally be modelled with equilibrium constant (hence for a weak complex), and Pitzer already pointed out this (and there is also a calculation in Riglet's thesis [90RIG] to link ion pair equilibrium constant with empirical pair interaction coefficient, i.e a tentative link between the two models). On the other hand several effect are certainly taken into account in the pair parameter, for this reason it is rather called empirical. Anyhow this gives a picture of the geometry on which are based the calculation of physics which gave SIT and Pitzer formula (the same type of calculations was used: resolving Boltzmann and Poisson equations, which gives the Debye-Hückel term, and using Taylor series expansion which give the virial terms). With this picture you can as well add a third cation in hydrogen bond cycles; but this addition should in principle modify the structure, or at least the energetics of each of its component, hence interaction terms for three ions should rather be used in place of (at least) some of the pair interaction contributions, and not added to it. In other words the competition between pairing equilibria is more appropriate than the ion multi (and eventually non interacting) layer picture that gives the virial expansion. On the other hand the enrgetics of this structure is of the order of magnitude of hydrogen bonding in water, hence very weak complex or activity coefficient, so this difference between the 2 approaches (competition versus addition of interaction) should not be detected experimentally. This means several sets of interaction parameters should in principle allow the description of the same system, and this indeed was published by Pitzer who typically showed correlation between the numerical values of its two empirical pair parameters. This finally should allow consistency between second toward third virial expansion: typically by fitting the pair parameters on single electrolyte (without any higher term, hence the pair parameter(s) does not only account for pair interactions) in a first step. In a second step you use experimental data involving exactly three ions, and you fit the three ion empirical parameters of higher terms, keeping the fixed values for the previous pair parameters, hence again the new fitted parameters have a mixed origin: they are not for three ions

interactions, but some of the previous two ion interactions are implicitly subtracted. The same procedure can be used also if you need to use empirical pair parameters for ions of the same charge: typically by choosing an arbitrary reference single electrolyte.

The previous discussion is only to say it is possible to add consistently new terms to the SIT formula. This terms are already added to the Pitzer formula, hence they are not automatically consistent with simplification of Pitzer formula into a second order (i.e SIT like) one (unless the above typical procedure have been used to obtain the Pitzer parameters, in other word unless a strong enough weight is given in the fit, to data were pair parameters are enough to model the data; and, when pair interaction parameters are used for ions of same charge, including data of the reference single electrolyte). We tested this (and the result was briefly reported in the Np/Pu draft) on your published Pitzer parameters: many of them are consistent with the SIT (i.e a third to second order simplification) while it seems some are not, specially for anionic Np(V) complexes. This does not mean your Pitzer parameters are incorrect: it means they are not consistent with the SIT formula. They could be at least for $NpO_2(CO_3)_i^{1--2i}$ for i=2 and 3 for which there is no need to use different anion-anion parameters in chloride and perchlorate media, hence they can be set to zero (in other words $NaCl$ and $NaClO_4$ are what I called above a reference electrolyte for this system).

_____

Nevertheless, the reviewer disregarded all these results.

PV 2j
Our review relied on your work in the selection of the standard complexation constants and solubility products for the $Na^+/Np(V)/CO_3^{2-}$ system (you are not discussing these numerical values). Only ionic strength corrections were not used (see PV 1a, b, g, h and i).

This comment is certainly rather due to an impression, than to what was actually written in an anyhow draft version, and anyhow rewording of the draft have now been performed to change this impression.

_____

Careful reading of our original papers might be sufficient to agree with our arguments.

PV 2k
Do you suggest we did not read carefully your papers?

This comment is certainly rather due to an impression, than to what was actually written: when we do not accept all your conclusions it does not mean we did not carefully examined all your arguments (since you are now repeating almost the same arguments, we have spent much time examining the same original experimental information many times). Despite your repeating of the same arguments give the bad impression you cannot produce new ones, neither you can answer ours, I can insure you we are re-examining all your publications in view of your comments each time we receive them.

_____

Several members of the NEA-TDB project groups required additional information and explanations, which hopefully will now be given in this manuscript.

PV 2l
What do you mean? Somebody is hiding information? Who? Several members are not able to read the information you are repeating?

_____

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.

PV 2m
Yes, hence you should not be annoyed that for checking and consistency our review performed a few reinterpretation and recalculation on your papers, and disregard some of your proposed values (actually only for activity coefficients) for which too many assumptions should be made to obtain consistency, while other consistent data are available

_____

Page 3
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.

PV 3a
Yes, we did not write it was not, or it was worst then in any other published study on the same subject (see PV2 c).

_____

Experimental procedure

All solubility experiments were performed in titration cells (see Appendix 1)... The Np(V) solid was precipitated in the titration vessel, and left aging 1 - 2 weeks before the experiment was started.

PV 3b

Hence it seems, it is the same experimental set up as I previously used with the help of Ingmar Grenthe and Diego Ferri [84VIT, 98VIT/CAP], but with different CO_2 partial pressure and several ionic strengths: Initial equilibration time seems shorter here, than in some other studies (but see PV 3c).

—————

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.

PV 3c

In my own experiments, we used 10 % to 100 % carbonic gas mixture, equilibration was usually achieved within 10 minutes, while rather a few days were needed to achieved solid liquid equilibration. I obtained the solid of correct stoichiometry within ata least about two months in similar experimental set up [98VIT/CAP].

—————

Maya [83MAY] reported in the experimental section of his paper:... Exactly the same observation was made in our studies and therefore the solubility experiments were started with a precipitate aged for 1 - 2 weeks.

PV 3d

Maya used batch experiments while you (and I) used open cells. I also used batch experiments and found equilibration was not yet achieved within 2 weeks (I used 4 and more 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.

PV 3e

After or before solid-liquid equilibration? Mine were from the filter used for sampling solubility measurements, hence usually after solid-liquid equilibration (see PV2 c and the corresponding figure).

—————

In contrast to the results given in [94NEC/RUN, 94RUN/KIM, 95NEC/RUN], Meinrath [94MEI] reported... a different x-ray pattern. However, he obtained comparable solubility data.

PV 3,4

This rather confirms what is written in our review: very similar (but not identical) diffraction patterns were obtained for compound apparently prepared in similar ways, and their solubilities (hence thermodynamic stabilities) were fond to be quite similar. Nevertheless according to the solubility product values you extrapolated to I=0 (at the end of your report under discussion), Meinrath's data can be considered as outlier (2σ threshold), which does not automatically mean his results should be rejected, but that he possibly had a different solid phase (which is consistent with x-ray diffraction pattern as you noticed). In principle it should be a fresh solid because it is more soluble (hence less stable, less aged) than others, however the difference is quite small and can partially be also attributed to systematic deviation between different labratories. Let us assume he really used a fresh compound, its x-ray diffraction pattern (PV 2c and the corresponding figure) can be attributed to a mixture of the solid initially prepared by Maya (and probably you), and mine: this can be consistent with ripening of the solid phase as discussed in our review (anyhow we did not rely on this observation in our review to draw any conclusion).

Finally your remark can induce a discussion that ends up with supporting our decision to select 2 solubility products, decision you are criticising below (without any more referring to this problem).

—————

(Page 4)

2) Slope analysis
As shown in [94NEC/RUN], the slopes of the solubility curves ($\log[Np]$ vs. $\log[CO_3^{2-}]$) are exactly -1

PV 4a

Certainly, not exactly: all experimental determinations have an associated uncertainty. Anyhow this confirms what is written in our review: smaller slope is not obtained when the solid phase is equilibrated a long enough time with the aqueous solution.

_____
...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

PV 4b

Yes, we never wrote neither thought it was a problem to extract equilibrium constants from your study. Evidence of compound with lower stoichiometry was indeed observed as intermediate in our study, while you did not report this information from yours hence both observations are correct and consistent. This might indicate that solid phases prepared by Volkov et al. have not been equilibrated a long time with aqueous solutions.

_____
3)...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 $NaClO_4$. Hence, the solubility data at I = 0.1, 1 and 3 M refer to the same solid phase.

PV 4c

Have you got the x ray characterisation? Over such a long period of time ripening of the solid phase cannot completely be excluded. If the time of equilibration is correlated with the ionic strength (0.1, 1 then 3 M) this could, in principle, induce systematic error on activity corrections fro the solubility product.

_____
And since the solubility data at I = 1 and I = 3 are practically the same as those obtained by Maya [83MAY]

PV 4d

Yes (despite different equilibration time and auxiliary data were used)

_____
and Vitorge [86GRE/ROB]

PV 4e

Not exactly.

_____
in the corresponding media (c.f. Fig. 1.1),

PV 4f

See also similar figures reported in [98VIT/CAP].

_____
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,

PV 4g

Your solid phase is identical to the one reported by Maya, or by Vitorge? In principle it cannot be to both of them because they do not refer to the same x ray diffraction pattern. On the other hand Maya did not published its diffraction pattern.

Anyhow our review did not rely on such discussion for selection of thermodynamic data because (i)enough solid phase characterisation information was available only from my own work (we did not, and still do not know when your solid phase was characterised and how often) and (ii)anyhow x ray gives an information on the structure of the bulk solid phase which might be different from the surface or any other undetected phase controlling the solubility. Discussion in our review is also based on kinetic observations.

_____
and not to different (more or less aged or hydrated) solids as concluded in the NEA review.

PV 4h

Not exactly, another conclusion can be deduced from your above remark and other observations (PV 3-4 4g and 5). Anyhow your affirmation is not a conclusion but a possible explanation for the (finally rather limited) differences in solubility product values between different laboratories. This type of difference is quite usual. Anyhow our review did not rely on such discussion for selection of thermodynamic data.

Fig1.1
PV 5

As in figures given in [98CAP/VIT], it is better to use different colours to point out data a priori excluded (see PV 2f, 5, 6c, 6e, and 8a) for extraction of equilibrium constants (figure at I=3M), and to plot all the experimental data. Otherwise, one might imagine you wanted to point out with this figure one set of data is more scattered than the other one, while in addition (to the previous remark) in your set you said you have excluded scattered data (which is of course correct, to extract equilibrium constants). Honestly did you mean this?

 The graphical presentation of the figure at I=1M is neither satisfactory because it seems Maya's data are on a single curve, while he showed a second series of slightly shifted for data after bubbling CO_2 in batches of the first series. He certainly attributed this to CO_2 because he also fitted an Np(V) hydrolysis constant of value not much consistent with later works. Hence the shift can also be attributed to ripening of the solid (the solid in the second series have been equilibrated twice). See PV 6d

In Vitorge's review
PV 6a
I will have problem with the co-authors!

_____
not a single sentence was written on... solid phase characterizations... Quite in contrast, he states and repeats several times that Kim and coworkers might have had chemical problems with the solid phase.
PV 6b
Our review did not criticise your solid phase (see PV 2c, 3a, e, 3-4 and 5), and relied on your work in the selection of the standard complexation constants and solubility products for the $Na^+/Np(V)/CO_3^{2-}$ system. Only ionic strength corrections were not used (see PV 2a, b, g, h, i, j and 4 g)

 This comment is certainly rather due to an impression, than to what was actually written in an anyhow draft version, and anyhow rewording of the draft have now been performed to change this impression..

_____
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.
PV 6c
This is only a matter of wording, this has been changed. We mainly wanted to say that all your published solubility data were at equilibrium (which is perfectly correct): you did not provide much information on the transient measurements, hence we cannot much discuss ripening of the solid phase from your publications. In the ongoing discussion you confirmed this, nevertheless you also claimed you did not had such problems with your solid phase: again it is a matter of wording (what do we call a problem? Hence I am not using this word in this sentence), in the ongoing discussion you gave extra information on the time needed to reach solubility equilibrium, this time is possibly quite consistent with previous experimental observations, hence with ripening of the solid phase (see also PV 2f 5, 6e, and 8a)

_____
...other authors (e.g. [83MAY, 94MEI]), who also reported Np(V) carbonate solubility data of comparable high accurcy.
PV 6d
Data reported in ref. [83MAY] are certainly less accurate than yours: Maya measured twice the solubility in some batches after a new equilibration time, he found slightly different solubility, and attributed this small difference to the effect of adding acid (CO_2 carbonic gas bubbled a short time in the batch) in the batch before the second equilibration period. I calculated from the information given in ref. [83MAY] and latter publish work on Np(V) hydrolysis, that this interpretation is certainly not correct, hence the small difference in solubility measured in Maya's publication is probably due to ripening of the solid phase, and this is consistent with the (relatively short) equilibration time he used (see PV 5).

 Accuracy of Meinrath's data is less clear, because there is not enough information to know whether and how he reproduced measurements.

————————

Non-equilibrium data are useless for the determination of thermodynamic quantities.

PV 6e

Yes; but they are of course useful to obtain kinetics information (typically ripening of the solid phase). Anyhow we never thought or wrote there was an equilibrium problem with your solid phase, and we used your data to select equilibrium constants.

————————

Page 7

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]

PV 7a

This assumption is in contradiction with experimental results: they are not particularly more scattered at low solubility (near the detection limit of ^{237}Np). In data from ref. [86GRE/ROB], see also more information on point in ref. [84VIT] and [98VIT/CAP], the scattering of data is clearly correlated with chemical information: equilibration time, quicker for dissolution than precipitation, much slower for the initial precipitation.

than the presence of different solid phases (which is the explanation given by the reviewer).

PV 7b

This explanation is supported by experimental data: kinetics (see PV 3a, 3c, 3-4, 4h, 5 and 7a) and X ray diffraction analysis, while your explanation is only an assumption.

————————

Lemire et al. [93LEM/BOY] mainly applied α-spectrometry... 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.

PV 7c

I do not thing so, I currently used α-spectrometry to measure ^{237}Np(V) concentration with a detection limit down to about 10^{-6} M, with no particular problem, with the type of procedure you described and 2 other ones. This is not particularly difficult: published works show detection limits down to less than 10^{-8} M. I never thought this could be a problem in Lemire's work, you must be very sure of what you are saying to put it in the forum discussion, and anyhow you could ask directly to the author on this specific points before initiating a public polemic relying only on assumptions. All along the review I never had such problems with Lemire: he never tried to extract more from his data, than should be, he rather had the reverse attitude.

————————

The accurate determination of the Np-237 concentration requires an additional α/β discrimination for the counts from Pa-233... If the LSC measurements are not corrected by discriminating the β-radiation from Pa-233,

PV 7d

Which is done by commercial apparatus.

————————

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.

PV 7e

Again "maybe". Again your assumption is incorrect. I had the necessary experimental set up. The α/β discrimination (by electronic discrimination of the form of the electric pulse, not by software which is usually not reliable) is very well known for a very long time (much before software and micro-computer existed) in CEA. Anyhow I did not use liquid scintillation but γ spectrometry at 29 keV (Pa has a pic at 83 keV). Anyhow Kim have all this information which is in CCE reports, because he was responsible of the contract, I do not know whether he showed you my semi annual reports, but I assume he read it in details because he was responsible of the contract and possibly because the same procedure as mines were reproduce in his lab. (the procedure is from Ingmar Grenthe for the cell experiments).

————————

Procedure to ascertain the equilibrium state

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.

PV 8a

This is perfectly correct, and confirms you did not provide the transient information as I wrote above (PV 2f 5, 6c and 6e).

_____

One can very well recognize, from jumps in the Np concentration, when the solid phase is aging

PV 8b

Solid phase transformation can be quite slow, specially with the time of at least several days (and actually several weeks) to transform the mono carbonato to the bicarbonato solid phase, I would not call this a jump. It is a matter of vocabulary.

       Ripening of the initial phase after the first minutes, is quite slow, not by jumps.

_____

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

...

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

...

The term A represents a correction for the differences in liquid junction potentials (ΔpH) and the trace activity coefficient of H $_+$.

PV 9a

It would have been better to have information on activity coefficients, independent from the liquid junction potential, for this you could have filled the reference compartment of your combined pH electrode with typically Na^+ 3M, Cl^- 0.01 M, ClO_4^- solution + AgCl solid. The slope is checked with a series of buffers at the same I (any I). 0.01 M H^+, Na^+, ClO_4^- 3M solution can typically be used for the calibration, additional checking with $CO_2(g)/HCO_3^-$ and HCO_3^-/CO_3^{2-} buffers.

_____

It is to note that Method B is applied by very many research groups... but also by Rai et al. [91FEL/RAI, 97RAI/FEL] and by other groups in the USA and in Japan.

PV 10a

In his last publication on Pu(IV) solubility in carbonate media, Rai wrote he considered his pH measurements at high I, not reliable, for this reason he used calculated pH. I calculated a shift of about 0.5 pH unit between calculated and measured pH.

_____

Unfortunately, our earlier publications [92NEC/KIM, 91KIM/KLE, 94NEC/RUN] contain illustrations of solubilities as a function of pH (-log of the H $_+$ activity), 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.

PV 10b

We used the numbers given in tables of your reports, and we fitted virtually the same equilibrium constants as the one you published. So it seemed we finally correctly understood your data.

_____

Question: correct or incorrect values of log [H $_+$] and log [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 NaClO₄, then the final result must be: log[OH $_-$] = -2.00

PV 10c

This example is not particularly well chosen because most glass electrodes should not be used (without further correction for alkaline error) at pH more than 10, and usually cannot be used at pH = 11 or 12 and above. at $\lg[OH^-]$ = -2, potentiometric titration is certainly the best way to obtain speciation. Similarly in carbonate studies speciation is in principle known as accurately from the concentrations of the buffer components (excepted when radiolysis or side reactions modify pH) hence pH measurement can also be considered as checking.

This was also done in my Np(V) studies and it is in the reports Kim had (and the primary information is now in [98VIT/CAP]: the titration points ($-\lg[H^+]$ vs. added acid) are on the calculated line, hence error in calibration, if any, is quite small in the cell experiments (bubbling 100 % or 10% CO_2) this is consistent with your remark on non nernstian slope for the glass electrode: possible systematic deviation due to non nernstian slope is expected at higher pH.

Since (at the high CO_2 partial pressure I used) NpO_2^+ is predominating in neutral to acidic media, possible error in the slope of the electrode in my work (which is not expected in this pH range) should have negligible consequence on the determination of my solubility product. This is further confirmed since after 2 a month equilibration, I obtained a slope of -1.04±0.07 (during the rest of the year) [98VIT/CAP], hence uncertainty on the pH measurement is within uncertainty of solubility data (I estimated independently reproducibility of my pH measurements to be of about ±0.06). This is further confirmed by the numbers you gave below (PV 11b and 15 e) for typical non nernstain slope for the glass electrode.

_____

Page 11

3) Comment on objections (Pierre Vitorge, Robert Lemire) concerning possible carbonate contamination in NaOH calibration solutions.

PV 11a

I do not remember we made such an objection: please give the exact citation and where you found it (it might be an error or unclear wording to correct in the Np/Pu draft)

_____

Comments on other pH calibration procedures

....

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 NaClO₄ solution.

PV 11b

Again assumptions: other laboratories (among them very old and well known ones in the field of solution chemistry) are supposed to have make an error in calibrating their glass electrode. This is a possibility, you need more cross verification (redundant measurements) and inter laboratory comparison to be more convincing (even if you are right).

However $-\lg[H^+]$ of CO_3^{2-}/HCO_3^- buffers are in the range of about 9-11, hence possibly 7 log unit from calibration fixed point (actually I usually did not used this procedure, but, after verification of the slope, I rather checked reproducibility with buffers in the pH range of my measurements); while for $HCO_3^-/CO_2(g)$ buffers $-\lg[H^+]$ are in the range of about 6-7 hence closest to the possible calibration point. Hence, possible systematic error due to non nernstian slope on the corresponding data is less important, which finally probably had negligible influence on solubility product determination (see PV 10c).

You wrote the slope of the electrode can be of 58.0 to 58.8 mV/pH unit instead of 59.16 mV/pH unit, hence a shift of 1.16-0.4 mV/pH unit error for the slope of one of your electrode, hence 0.0196-0.0068 /pH unit in CO_3^{2-}/HCO_3^- buffers the error should then be of
0.14-0.05 log unit,
while in $HCO_3^-/CO_2(g)$ buffers the error should then be of
0.10-0.03 log unit.
This confirms (PV 10c) that this error should be within uncertainty for experimental determinations in cell under $CO_2(g)$ 100°% bubbling as I used to measure my solubility product (see PV10 c and 15 e)

_____

Page 12

Vitorge et al. [86GRE/ROB, 90RIG] calibrate their electrodes in the acidic range with HClO₄/NaClO₄ 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.

PV 12a

Again assumptions: ask me what I did before starting a polemic. The slope of the electrode used in my Np(V) solubility study, was also checked with independent buffers at low I. The difference with the theoretical slope was within the reproducibility (0.06 pH), which finally seems quite consistent with your above discussion on slope, and anyhow would induce a maximum possible systematic error within uncertainty for my experimental determination of the solubility product (PV 10c and 11b).

_____

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.

PV 12b

This was only discussion in the case you wanted to change TDB auxiliary values: in that case redundant measurements, cells with no liquid junction and inter laboratory comparison would of course be required.

_____

Page 13

H_2CO_3 dissociation constants in NaCl and $NaClO_4$ solution

Page 14

Page 15

all literature data shown ... were determined with glass electrodes calibrated only in the acidic range, and extrapolated to the alkaline range by assuming ideal Nernst slopes.

PV 15a

This is your basic assumption. you wrote a 44 pages document, where you basic assumption is in less than a sentence, within 2 lines. You could have given more details, typically as we do in the TDB review in Appendix A (typically give the slope you imagine the electrode had, and possibly try to find out whether it is realistic for material eventually used at that time). Your assumption is possible.

_____

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.

PV 15b

You must be very sure, to say this. More verification of your above assumption, is certainly required, before deducing such conclusion.

Repeating 4 times the word "mistake" give the impression of insisting, repeating your judgement, rather than be able to give clear enough argument, that the reader will deduce the conclusion by himself. This style is sometime needed for reports given to persons that take care of science but are not doing themselves science, it is not convincing for scientist of the field

_____

This mistake

PV 15c

You decide it is a mistake, while it is only an assumption to explain inconsistent data between your laboratory and much published work (as you wrote), hence it is certainly more appropriate to write "possible systematic deviation" This wording also avoid moral judgement.

_____

is illustrated... example is taken from our FZKA report

PV 15d

You are not showing what was done in other laboratories; but modelling what you assume was their systematic error. Hence this does not demonstrate they actually made or not this approximation; but only that your explanation is possible. You do not need to convince us of this, because before you comments, we had already written in the draft it might be possible auxiliary data selected in our review, need reevaluation. I also evaluated above (PV 11b) what would be the maximum possible systematic error according to your interpretation: this is rather more useful to discuss whether such possible deviation can account for observed discrepancy... and this depend on the pH range and the methodology used.

_____

...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)... the value of log K_2 is determined in a solution with the composition:

0.05 M $NaHCO_3$ / 0.05 M Na_2CO_3 / 2.85 M $NaClO_4$

...the dashed line for electrode calibration, the value of log K_2 = -9.64

...consistent with the literature data and with the auxiliary value of -9.62 from the NEA-TDB.

- the solid line ...log K_2 = -9.81.

the errors in log K_2 are about 0.1 - 0.2 log units.

PV 15e

OK, this is interesting and confirm you have a possible explanation. Nevertheless try more confirmation: again find a way to have redundant measurements, typically use commercial buffer in the whole pH range between your calibration and working points ($lg[H^+]$ = -2? and -9.8). Do together the calibration in NaCl and $NaClO_4$ media (you possibly have already done this) in that way pollution of the NaOH is less probable, look for alkaline error (in that case the slope would not be constant: it decrease at high pH)...

You found a shift of

0.17 pH unit

which is consistent with twice the error I evaluated above (PV 11b) from your non nernstain slope information. Similarly the deviation for lgK_{p1} with the same electrode should be of

0.06

which is of course consistent with what I wrote above (PV 10c and 11b): this is within uncertainty for my determination of the solubility product.

_____

Page 18

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

In the Np/Pu draft, the reviewer is irritated,

PV 18a

Our review wrote a remark, it is your interpretation to deduce a reviewer was irritated which is not supported by the way this remark was done and written. Anyhow within our review team, irritation was not an argument accepted to write a remark.

_____

because the Np(V) carbonate solubilities of [91KIM/KLE, 94NEC/RUN] and those of [83MAY] are in good agreement, although considerably different constants

PV 18b

Different, not considerably different.

_____

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 $NaClO_4$)

PV 18c

There is very good agreement with those in ref. [83MAY]; but not with those in ref. [86GRE/ROB]. The error in pH calibration might cancel as you wrote below depending on the way Maya actually checked his electrode, beside this (from the information you gave in the course of the present discussion) its equilibration time might have been shorter than yours (see PV 3d, 3-4, 5, 6d, 18c and d).

_____

 is of course not accidently as supposed

PV 18d

Not exactly supposed which rather means we adopted this hypothesis in contradiction with what is written in our draft and you reproduced above (PV 18c).

_____
 by Vitorge in the NEA review.

PV 18e

I am not the only author of the NEA review. I have published some of the draft of my contributions, so you should rather refer to it, despite I might have changed my mind (typically after discussion within the review team) or do new calculations since.

_____
 This is demonstrated below

PV 18f

When you make assumptions (as in most parts of this document) what you can usually demonstrate is that it does not lead to any contradiction with available information, hence that it is a possible explanation; but you usually cannot validate it.

_____
 for a carbonate solution in 3 M $NaClO_4$....Vitorge et al. (ideal Nernst slope)

PV 18g

Again an assumption: I indeed checked the slope and found that in my working domain, it was the theoretical slope within uncertainty, but I rather stuck on the NEA value the closest to my working conditions. Anyhow the possible systematic error as estimated from your number should be within reproducibility of pH measurements and experimental uncertainty for the determination of the solubility product under discussion (PV 10c, 11b and 15b)

_____
 and Neck determine a considerably different H^+ concentration.

PV 18g

Different, not considerably different. You calculated above this difference could be of about 0.2. Elsewhere in the draft we wrote that two of your experimental determinations for the $\log_{10}$ of an equilibrium constant were inconsistent within your stated uncertainty, you complained because you said they only differed by 0.2 $\log_{10}$ units. So in one case this is considerable, and in the other one it is not (actually it is not).

_____
However, because they apply different H_2CO_3 dissociation constants... they finally obtain practically the same (correct) values of log [CO_3^{2-}].

PV 18h

In other words, possible systematic deviation should cancel, I agree with this; nevertheless it, in principle, depends on the procedure used for calibration. Anyhow I made several assumptions (where was the fixed calibration point? Which slope was used?) I came to the same conclusion: the influence of this systematic deviation on solubility product under discussion, is within uncertainty (PV 10c, 11b and 15b).

_____
=> General comment on "recalculations" of solubility or complexation constants for actinide carbonates
...in the NEA reviews there are often recalculations of original data...

_____
Page 19
...The authors XY used the constant of log x to calculate the CO_3^{2-} concentration...
In many cases such recalculations do not correct the original data. Just in contrast - they make them incorrect,

PV 19a

Recalculation is usually performed, not specially to use other auxiliary data; but to check the numerical treatment and in a few cases, for sensitivity analysis. As written above (PV 18h), I rather used the assumption that the systematic error should cancel. You can typically see that the equilibrium constants I recalculated from your experimental measurements, are usually virtually the same as the data you published

_____

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),

PV 19b

This is already discussed above, this is one possibility among others. From what you wrote above, it actually comes out that all the pH measurement in this media are incorrect, excepted yours, pointing out only one of these measurement, rather gives the impression you are not able to objectively write on the subject, and that your main goal is personal resentment, this actually is not much convincing from this point of view. My results are, in addition, a bad example for your demonstration for 2 reasons: (i)I rather used published auxiliary data hence the discussion should be for the corresponding publications (not mine) (ii)I also calculated the potentiometric titration curves for the experiments at 0.10 to 1 atm of carbonic gas, which model quite well the measured pH this is shown in CCE reports that Kim have (or at least had) and the needed information is anyhow published in a CEA report. This is also a checking of my pH calibration. This checking does not contradict your above discussion on slopes (PV 10c, 11b, 15c).

_____

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.

PV 19c

Again you are making assumption on what was done, in that case it is clearly incorrect, see PV 19a.

_____

And hence they lead to incorrect results !

PV 19d

Give numerical examples. the values I recalculated are usually virtually the same as the ones originally published.

_____

Page 21

2.1. General comments on shortcomings of the SIT

…However, it is inacceptable that shortcomings and limitations of the SIT are simply ignored,...

PV 21a

Limitations of the SIT formula are well known from the beginning of its using.

_____

(1) erroneous chemical conclusions are drawn and incorrect thermodynamic data are selected because of these shortcomings

PV 21b

Activity coefficients are usually a small correction, usually even smaller than the scattering of experimental data, specially when from different laboratories, only in special difficult cases it can induce such errors.

Beside this, the possible systematic deviation on the solubility product under discussion is within uncertainty as estimated from the numerical information your are giving in your comments (PV 10c, 11b and 15c).

_____

(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.

PV 21c

Your experimental data were not ignored, they were used with the same weight as data from other laboratories to select thermodynamic values in our review. Only your activity coefficients were rejected, this has nothing to do with SIT or Pitzer formula: just because we extracted internally inconsistent values for activity coefficients, from your experimental data: your liquid-liquid extraction data are inconsistent with your solubility product data, when using TDB methodology: $\varepsilon(NpO_2^+,ClO_4^-)$ values in, at least, the range 0.18 to 0.34 kg.mol.$^{-1}$ was calculated in our review, the mean is 0.25, the TDB value is 0.25±0.05, the value you propose is 0.20. To resolve your contradiction you had to develop a new methodology, adding new empirical terms and fitted parameters for data at high I, while the aim of thermodynamic data bases is usually to provide values at I=0. Anyhow the new methodology you proposed does not seem to rely on enough experimental confirmations, and the way you used it up to now is not enough consistent with the TDB methodology (see PV 2i)

_____

Limitations of the SIT

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

PV 21d

This is known, used and written in the TDB guidelines and books from the beginning. This I range is enough for most of the published data. Anyhow the aim of the review is to select data at I=0, not to provide a formula to extrapolate them to very high I.

_____

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

PV 21e

This have practical low importance. One does not know accurately the behaviour at low I, because accurate measurements are more difficult. The idea of the SIT formula is to give an explicit and reproducible way to extrapolate data to I=0, not to give the good corrections to pure water which nobody knows up to now. Pitzer formula is not better, and this is already published: you need data at low ionic strength to fit one of the second virial parameter, unfortunately you often do not have such data for complexes, hence the fitted low I parameter is not well defined, neither is the result at I=0. Some authors who recognised this type of limitation (not enough accurate data in the good I range to fit all the parameters) usually fix one parameter or use other approximations, some of them are perfectly correct; but you end up with a formula no more accurate than the SIT formula. Note that both formula are empirical, their fixed parameters or functions were fitted on experimental data (usually isopiestic ones). Finally there is no good universal approach (see also PV 2i).

_____

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

PV 21f

There are not (or very few) direct experimental evidence of such interactions. And you tretment is not enough consistent with the SIT (see PV 2i and 21c).

_____

the scientific problems do not arise as a question of SIT or Pitzer modelling - they arise from experimental data!

PV 21g

This was already written in our draft, before your comments. Please avoid writing 44 pages on "objections" on which we agree.

_____

Pitzer modelling performed ...only ... in order to demonstrate the errors coming from the oversimplification of the SIT procedure.

PV 21h

See above, each formula has its draw back. One advantage of Pitzer formula is it has three times more parameter to fit, among which even one at low I where there is no experimental evidence that there is any difference between different electrolytes of same stoichiometry. This advantage can become a disadvantage since you can simply fit the errors, which you possibly did since, as mentioned above, you published data from which inconsistent activity coefficients can be extracted, nevertheless I did not try to calculate whether this propagates error on other activity coefficients. (see also PV 2i and 21e)

_____

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

PV 21i

Again, not considerably different: different. This can also be seen directly by comparing the values for the acidic constants in both media.

_____

These differences cannot be described with the simple SIT approach used in the NEA

PV 21j

You are right: there is only one empirical parameter for each pair of anion-cation. You could as well add new terms to the SIT formula (PV 2i), typically using a third (instead of second) virial development which would result in empirical parameters for 3 species (hence at least 2 of the same charge), for consistency it would then also be needed to use pair empirical parameters for ions of the same charge. This was not done for a series of reasons: one is simplicity (typically the present SIT formula is symmetrical for each pair) hence avoiding too many parameters which would require more experimental data than available; a second series of reason is that there is no experimental evidence that such parameters are needed, excepted in the 2 cases you pointed out. Hence the discussion should first be on the experimental results corresponding to these two cases. The first case is the above difference in your measurement of the carbonic acid constant between NaCl and NaClO$_4$ media, as discussed above, you might be right, but experimental confirmation is still needed. The second case is discussed below, it is for Np(V) system, you claimed such mixed empirical parameters are needed for all the anionic Np(V) carbonate complexes, while there is experimental indication only for the first one and again experimental confirmation is still needed, at least because inconsistent values for the activity coefficient of the aquo cation can be extracted from your experimental measurements (solubility and liquid-liquid extraction).

  If these experimental confirmation will be obtained, it would be straightforward to add the extra terms and fit the corresponding parameters (PV 2i).

_____

Page 22

_____

(However, these interactions are not zero,

PV 22a

Not exactly, experimental confirmation is needed: hence "might not be zero..."

_____

two further corresponding examples

PV 22b

This is a good idea to look for further examples. As you wrote it is better using data for which reliable experimental information is available. Nevertheless I will not discuss your examples, because it would first be needed to review the experimental data which is out of the field of the present discussion. Just one comment: it is better to compare the experimental data than Pitzer parameters, because you usually obtain triple interaction parameters even if they finally cancel when using them for modelling the original experimental results. This because there is not usually a unique set of Pitzer parameters than can be fitted on a single system: Pitzer parameters are correlated as pointed by Pitzer in his earlier publication, this is the drawback of having so many empirical parameters (see also PV 2i).

_____

Page 23
Fig.2.1

PV 23a

This figure essentially provide new information as compared to figures 1.4 (it is not "a new proof", but a combination of figures 1.4)

_____

Page 25
Neptunium(V)
Solubility constant for $NaNpO_2CO_3 \cdot xH_2O(s)$
In the NEA review, the results of Kim and coworkers... were generally critisized to be not reliable and disregarded

PV 25a

These data were used to select the standard equilibrium constant of the Np(V) carbonate data, hence they are not disregarded. Only your activity coefficients were disregarded. As already said from the beginning and in my e-mail to Fhanganel in 1997, the reason is that inconsistent values for the activity coefficient of NpO_2^+ are calculated from your own data using TDB methodology, hence we neither used the other data.

_____

...this is a pure arbitrary act of the reviewer,

PV 25b

A review is always no more than the opinion of the reviewers (not reviewer actually), in this particular case it is not arbitrary (see the reason just above: PV25a).

―――――――

The evaluation of the solubility constant at I = 0 is primarily based on solubility studies of Maya [83MAY] (in 1 M NaClO₄) and Vitorge (in 3 M NaClO₄)

PV 25c

You forgot one study: your own solubility data extrapolated to 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

PV 25d

Not only, the main reason is difference in equilibration time. Maya did not published its X-ray diffraction pattern; but if we accept what he claimed, his diffraction pattern was not the same as in my work. So the conclusion is not specially based on the values of the solubility products; but rather on kinetics observation (see also PV 3d, 3-4, 4d, 5, 6d, 18c and d).

―――――――

Page 26

―――――――

Fig. 2.4

PV 26a

Several interpretations can be given for this figures, but it is clear that all data in NaClO₄ media are consistent within uncertainty considering usual possible errors for such systems: ripening of the solid and different calibrations procedures between different laboratories. The figure is not well chosen to compare data in NaCl and NaClO₄ media, because the activity coefficient of NpO_2^+ cation, hence $\Delta\varepsilon$ values in both media are expected to be different.

―――――――

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

PV 26b

Again, it is not an assumption, but the result of x-ray diffraction study.

I performed the same calculation from your data: at I=0.1 to 3 M

$\lg Ks° = -10{,}954 \pm 0{,}14740043$

$\Delta\varepsilon' = 0{,}233 \pm 0{,}070$

$\varepsilon(NpO_2^+,ClO_4^-) = 0{,}335 \pm 0{,}100$

where uncertinty is 1.96 standard deviation

$\varepsilon(NpO_2^+,ClO_4^-) = \Delta\varepsilon' - \varepsilon(Na^+,ClO_4^-) - \varepsilon(Na^+,CO_3^{2-}) - 3.5\,[a(H_2O)\,/\,m]$, the last term is an approximation for water activity

$\varepsilon(Na^+,ClO_4^-) = -0.01 \pm 0.01$

$\varepsilon(Na^+,CO_3^{2-}) = -0.06 \pm 0.06$

$a(H_2O)\,/\,m = -0.015 \pm 0.01$

These three last values are calculated from Pitzer parameters given in your publications or Pitzer's; but with no mixing term, the idea was only to be as much consistent as possible with your data (hence not using TDB auxiliary data). The only difference with TDB auxiliary value is $\varepsilon(Na^+,CO_3^{2-})$ is bigger by 0.02 kg.mol⁻¹, hence you can decrease $\varepsilon(NpO_2^+,ClO_4^-)$ by 0.02 kg.mol⁻¹, which anyhow is within uncertainty.

On your Fig2.5 page 27, you obtained a little more than -11.0 for $\lg Ks°$ which is consistent with the value I calculated. You wrote below this figure $\Delta\varepsilon = 0.29$. From my above values I calculate $\Delta\varepsilon = \varepsilon(NpO_2^+,ClO_4^-) + \varepsilon(Na^+,ClO_4^-) + \varepsilon(Na^+,CO_3^{2-}) = \Delta\varepsilon' -3.5\,[a(H_2O)\,/\,m] = 0{,}285$ which is the same value as yours. You wrote on the figure $\varepsilon(NpO_2^+,ClO_4^-) = 0.20$ [95NEC/FAN], while from $\Delta\varepsilon'$ I obtained

$\varepsilon(NpO_2^+,ClO_4^-) = 0.335 \pm 0.099$

which is different. It should not be since our $\Delta\varepsilon$ values are consistent. This is a bit misleading: the choice of 0.20 is not much consistent with TDB methodology as used for your solubility product.

From your liquid-liquid extraction data, I obtained

$\varepsilon(NpO_2^+,ClO_4^-) = 0{,}182 \pm 0{,}013$

which is neither consistent with TDB methodology, nor with you solubility data.

Page 28 you wrote this inconsistency in your own data can be resolved by using $\varepsilon(Na^+,CO_3^{2-}) = +0.04$ instead of -0.06 (as I used above, or -0.08 which is the TDB auxiliary value): this results in the value of

$\varepsilon(NpO_2^+,ClO_4^-) = 0.24$ (± 0.07 at least: or more depending the uncertainty you attributes to $\varepsilon(Na^+,CO_3^{2-}) = +0.04$) (and not 0.20) instead of 0.335 ± 0.099. 0.24 is virtually the TDB value (0.25); is still different from the value $\varepsilon(NpO_2^+,ClO_4^-) = 0{,}182 \pm 0{,}013$ extracted from your liquid-liquid extraction data. This last inconsistency will be

discussed below; hence the discussion is now on $\varepsilon(Na^+,CO_3^{2-}) = +0.04$ instead of -0.06. Your explanation might be correct, but there are still two apparent inconsistencies:

1. isopiestic measurements rather gives a negative value for $\varepsilon(Na^+,CO_3^{2-})$
2. from your Pitzer parameters I also obtained a negative value for $\varepsilon(Na^+,CO_3^{2-})$

Both inconsistencies can be resolved; but quite in a contradicting way unless you add a new parameter. The first one refers to high carbonate concentration where activity coefficients could be different from trace activity coefficient (as it seems you suggested). To deduce trace activity coefficients from Pitzer parameters obtained at high concentration, one possibility should be to use only the ion pair empirical terms and parameters (PV 2i). It is what I did and end up with the second inconsistency. Conversely you can object I only used the ion pair empirical terms and parameter to calculate $\varepsilon(Na^+,CO_3^{2-})$ from your Pitzer parameters; but in that case you cannot resolve the first inconsistency... Finally it seems you added an empirical term and a parameter for the (ClO_4^-,CO_3^{2-}) pair. This is mathematically correct, but this can also be interpreted as adding a new parameter because the existing model cannot predict a new set of experimental observations: your conclusion is the existing model is indeed incorrect, the opinion of our review is either the existing model is too limited, or the new sets of experimental measurements are incorrect. For this reason we did not use your activity coefficients.

You provided further liquid-liquid extraction experimental results which is a good idea to have independent confirmation: From your liquid-liquid extraction data in 0.2 to 3 M NaClO$_4$, I calculated
$\varepsilon(NpO_2^+,ClO_4^-) = 0,182 \pm 0,013$
this value is inconsistent with value I calculated above (0.335 ± 0.099) from your solubility data; but is consistent with the value $\varepsilon(NpO_2^+,ClO_4^-) = 0.24$ (± 0.07 at least); but is not consistent with the TDB value (0.25 ± 0.05). In your liquid-liquid extraction data, there was only one anion, hence no eventual anion-anion parameters. The same was true for the electrochemical and isopiestic measurements used to select the TDB value, hence I see no way to resolve this last inconsistency.

However since we have a data (actually 2 inconsistent ones) with no anion-anion parameters we should use them to select a value for $\varepsilon(NpO_2^+,ClO_4^-)$ as explained above (see also PV 2i) to keep consistency with simplified formula, i.e without triple or anion-anion term, i.e the actual SIT formula (that you want to extend with these extra terms). First possibility you take the TDB value (typically because all this is to obtain consistency with the TDB), hence you decide there is an experimental error or an over simplification in the data treatment of your liquid-liquid extraction study, the drawback of this, is since you published eventually erroneous activity coefficient, our review might prefer to avoid using all your activity coefficients. An alternative would be to use the value extracted from the liquid-liquid extraction data; but since it is not consistent with the TDB value, our review would reject this interpretation. Alternatively you proposed a sort of compromise, a medium value of 0.20: this is a possible solution, but it is finally supported by less clear experimental evidence, than the existing value. It seems new experimental determinations are needed for binary system. I see two of them: isopiestic measurements and NpO$_2$OH(s) or Np$_2$O$_5$(s)solubility product. I think you have data for this system: can you extract a value for $\varepsilon(NpO_2^+,ClO_4^-)$ from the hydrated hydroxide (or oxide) solubility product? On the other hand the solid phase is even less well defined than from the carbonate solid, hence the effect of activity coefficient might be less than the scattering of the data.

Anyhow, the influence of triple terms for the activity coefficient of typically the limiting carbonate (anionic) complex is not negligible, while there is no difference in its activity coefficient in sodium chloride and perchlorate media. As explained above, to keep consistency with the (pair) SIT formula the triple terms should be set to zero, as they should in all the similar cases of your interpretation to improve consistency with TDB.

Note that to resolve your contradictions, you need to add a new empirical term and a fitted parameter, even adding this you end up with values for $\varepsilon(NpO_2^+,ClO_4^-)$ with associated uncertainty bigger than the value selected in our review (0.25 ± 0.05). In addition you introduced this new empirical term and a fitted parameter to fit experimental determinations of carbonic acid constants in NaClO$_4$ media discussed elsewhere in your comments. More experimental evidence is also still needed on this specific problem, i.e to confirm experimental evidence of the need of anion-anion or triple terms and empirical fitted parameters. For these reasons, we cited your interpretation and said from the beginning (before your started this polemic) it might possibly be correct: some TDB auxiliary values might need revision; but more experimental evidence is needed, conversely it cannot be ruled out there is an experimental error in your measurements.

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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 $K^\circ_s = -11.0$ ± 0.2.

PV 27a

As above, uncertainty is 1.96 σ. In the calculation below I entirely attributed to activity coefficient, shift from NaCl media to ideal pure water. This is consistent we the decision of our review not to consider any Np(V) chloride complex, while it might not be with your other publications where you determined chloride complexation constants for Np(V), nevertheless it seems you also used the same assumption as in our review (hence possibly inconsistent with your published interpretation for your other measurements), therefore we used the same assumption and finding the same numbers will indeed mean we agree on these numbers.

From your liquid-liquid extraction data in 0.2 to 3 M NaCl, I calculated

$\varepsilon(NpO_2^+, Cl^-) = 0,067 \pm 0,013$

which is rather consistent with your value

From your solubility products in 0.1 to 3 M NaCl, I calculated (as above in NaClO$_4$ media)

$lgK_{so}° = -11,01 \pm 0,26$ which is consistent with your value (-11.0), and the value I calculated above in NaClO$_4$ media (-10,95 \pm 0,15)

$\Delta\varepsilon = -0,00 \pm 0,07$

From $\Delta\varepsilon = -0,00 \pm 0,07$, I calculated:

$\varepsilon(NpO_2^+, Cl^-) = 0,09 \pm 0,10$

which is consistent with your above value (0.09), and the value I calculated from your liquid-liquid extraction data (0,07 $\pm$ 0,01)

Hence we agree on the calculation (even if we eventually do not present them in the same way) in NaCl media. I found inconsistency between data extracted from the results of your measurements using two different experimental techniques in NaClO$_4$, but not in NaCl media. Different explanations can be given for this; typically (non of them can be proven (excepted eventually the first one)):

-I made an error in my calculations or in interpreting your data in NaClO$_4$ media,

-activity corrections are less important in NaCl than in NaClO$_4$ media, consequently possible systematic error is within uncertainty in NaCl but not in NaClO$_4$ media,

-there is a true chemical or experimental difference in both media (in typically the liquid-liquid extraction systems, or the solubility studies, typically non negligible difference in ripening of the solid phase in the NaClO$_4$ work, but not in the NaCl one, impurity in NaClO$_4$...)...

-and off course your above explanation (need of extra empirical term and anion-anion fitted parameter) but it does not seem it provides consistency for your liquid-liquid extraction data in NaClO$_4$ media.

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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 NaNpO2CO3 . 3.5H2O(s) described by Volkov et al. [77VOL/VIS] and Maya [83MAY].
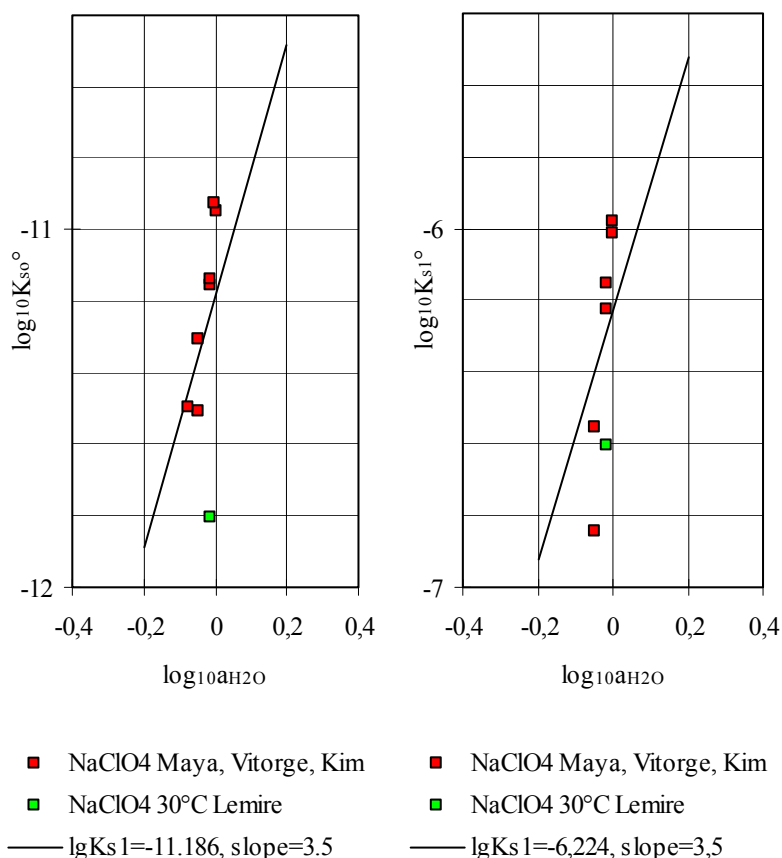
PV 27b

The x-ray diffraction patterns published in [77VOL/VIS] and [95NEC/RUN] are the same, but I do not know whether they correspond to samples prior or after the achievement of equilibrium solubility

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and Maya [83MAY].

PV 27c

That is what he said in his publication, but the x-ray diffraction patterns were not published (see also PV 3d, 3-4, 4d, 5, 6d, 18c and d), and it seems it was for an initial solid phase, while equilibration time was relatively short, and his two series of measurements can be interpreted as evidence of ageing of the solid phase (but this interpretation cannot be proven. I also tried correlation with water activity because Volkov et al. interpreted similar variations in the x.ray spectra as observed from those published with solubility data, with variation of the hydration of the solid compounds; but this effect on the solubility is probably less important than other reasons for the scattering of the data (see the figures)

NaClO4 Maya, Vitorge, Kim	■ NaClO4 Maya, Vitorge, Kim
NaClO4 30°C Lemire	■ NaClO4 30°C Lemire
—— lgKs1=-11.186, slope=3.5	—— lgKs1=-6,224, slope=3,5

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(Solely Meinrath [94MEI] reported an other (hexagonal) modification of $NaNpO_2CO_3 . xH_2O(s)$, with different x-ray pattern).

PV 27d

X-ray spectra published by Meinrath can be interpreted with a mixture of the solid phase you prepared (or obtained after solubility equilibration?), and the one I obtained after solubility equilibration. (see the figure referred in PV 2c)

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Page 28

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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].

PV 28a

This is a possibility; but only one possible interpretation (see PV 27a)

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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].

PV 28b

There is no determination of x = 3.5 in ref.[83MAY], only the indication that he prepared a solid compound of x-ray diffraction pattern consistent to a published one of x = 3.5. Realistic structures have been proposed for this type of solids; but they cannot be proven.

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(with the exception that $\varepsilon(NpO_{2\,+}/ClO_{4\,-}) = 0.20$ is used, instead of 0.25 as proposed by Vitorge,

PV 28c

The value of 0.25 is the TDB auxiliary value, it was selected in the Uranium book (because the methodology had been first validated on Uranium), and confirmed in our review, it is actually from Riglet's thesis (who was my student), see also PV 27a.

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Remember: ε(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).
PV 28d
Not exactly, it is your proposition; but, as discussed above, more confirmation is needed.

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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

Pages 28-29
PV 28-29
From your calculations it appears that SIT and Pitzer treatments gave standard values for the solubility product in a range of ±0.19 and 0.10 respectively (-10.96±0.19 and -11.06±0.10, uncertainty is 1.96 σ), hence Pitzer's treatment gives smaller uncertainty and smaller range of values, but more empirical parameters (than in the SIT formula) were used. However, all the data are from the same laboratory: this is an important (for our discussion) difference with the data in NaClO$_4$ media.

In NaClO$_4$ media the range is ±0.74 and 0.37 respectively (-11.215±0.58 and -11.09±0.28), as for data in NaCl media Pitzer's treatment gives smaller uncertainty and smaller range of values, more empirical parameters were again used, in addition you also had to add an extra fitted parameter as compared to the treatment of data in NaCl media. Note that anyhow, while there are more experimental data in NaClO$_4$ media and more fitted parameters in the Pitzer treatment, the range of values is bigger than in NaCl media which is quite expected (data are no more from the same laboratory here), but statistical uncertainty is also bigger, while the contrary would be expected from a statistical point of view, if in both media uncertainty of each experimental determination was the same. One logical assumption (which cannot really be demonstrated) is of course that uncertainty is less important in NaCl media because all the data are originated from the same laboratory... In other word typically differences in auxiliary values and/or calibration procedures are usual. Nevertheless it cannot also be ruled out from a statistical point of view, that the extra fitted parameter you introduced (for "anion-anion interactions") actually fit this type of inter laboratory systematic deviation or other chemical problem.

Anyhow X-ray diffraction patterns (figure attached to comment PV 2c) indicate the solids used in 2 of the studies were, or might have been different form the other ones. These two solids should be closer, while they surprisingly gave the maximum and minimum solubility products. Disregarding these two data in NaClO$_4$ media, one obtain -11.21±0.46 and -11.10±0.21 in NaClO$_4$ media. This time all the data are from the same laboratory (yours), excepted Maya's one which is in agreement with yours, there are still more data than in NaCl media, nevertheless statistical uncertainty is still more important.

You have a consistent interpretation for all the data; but these discussion indicate a small statistical problem, hence possibly originated in chemical or other problems (or maybe there is not enough data to support the statistical discussion). This was in part expected because inconsistent results were at high ionic strength, and you added an extra empirical term and a fitted parameter to solve this problem.

Your treatment also showed there is no difference (within statistical uncertainty) between the standard values of the solubility products determined from data in chloride and perchlorate media. Again this is not really new because we saw from the beginning at I=0 (or as you pointed out at low I) there is no problem. Your point is that a single solubility product is enough to interpret all the data, this is correct: there is no statistic outlier in the overall series (NaCl + NaClO$_4$) using a 1.96σ threshold, nevertheless in the NaClO$_4$ series (treated alone) there is one outlier ([94MEI]). I also checked this on the values I reinterpreted, the numbers are not much different, Meinrath's value can still be considered as a statistical outlier; but this time mine too, and since its solubility product is less than the others, this would mean in principle that it corresponds to the most stable solid, hence the value could be selected (instead of the mean of less aged solids); but I would not rely on this analysis because the 1.96σ threshold is quite arbitrary. If now we add the values reported in ref. [93LEM/BOY] at 30° (or the result of reinterpretation of this study, in our review), it is an outlier: from a statistical point of view, and it correspond to an even more stable compound than the one I prepared, and for chemical reasons it corresponds to a very interesting study that showed evidence of solid phase transformation.

Now what is the consequence of this: our review had a first possibility that was to choose a single solubility product. Actually this was really discussed, and for a time proposed in the course of the review. The value could be any of the values discussed above (typically -11,15±0,59): they are all within statistical uncertainty. According to the methodology adopted in our review for estimation of uncertainty, we should not select in this case the statistical uncertainty, because there is experimental evidence of changes in the solid phase, hence uncertainty should have

covered the whole range of published values and possible associated uncertainty and systematic errors. This was of course not much satisfactory, because one of the main reason for this relatively big uncertainty was not much consistent with thermodynamics: if the solid phase was changing, the selected value should correspond to the most stable phase, hence the less soluble: the smallest solubility products. This type of discussion was not specific to this solid/liquid system, and we choose one of the usually adopted solution in our and previous TDB review. Our solution has also its drawback, but is more consistent with experimental observations..

Anyhow this decision of selecting two solubility products is finally quite independent from the above discussion on activity coefficients and pH calibration, because its rely on direct experimental qualitative evidence. It might even be reflected in your numbers because, as discussed in our review, several solubility product values seem to be logically correlated with their time of equilibration: from your numbers, as from the ones used in our review the most stable solid at room temperature is the one I prepared, and anyhow the one prepared by Lemire at slightly higher temperature (30°C) is even more stable. On the other hand it is not clear whether this difference between solubility product values, are more than possible systematic deviation between methodologies used in different laboratories.

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Page 31
PV 31
The discussion of the second Np(V) solid phase is quite similar as above, hence I do not repeat it.
I have the additional comments:
- Instead of discussing K_{so} value, it is better to discuss K_{s3} value which is directly determined experimentally, while K_{so} value has to be deduced from thermodynamic cycle.
- another advantage of K_{s3} is that it involves only one Np(V) aquo ion, and you more easily discuss ionic strength corrections, specially you see there is no difference between chloride and perchlorate media for the limiting complex (you also see it directly on the solubility curves). For this reason it is quite artificial to discuss (again) NpO_2^+ activity coefficient in this part: this species is only introduced in the thermodynamic cycle you implicitly used to deduce K_{so} from K_{s3}, hence it is certainly better to performed this part of the cycle at I=0 avoiding propagation of the errors originated in the uncertainty of the activity coefficient for NpO_2^+. This is more or less what you wrote, but did not use in your calculation.
- you did not mentioned the very important work of Simakin.

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Pages 32-34
I am not discussing Am and U: the review is already published

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Page 35
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.
PV 35a
We used another procedure in our review: simply excluding activity coefficients originated from studies were systematic errors could not be ruled out... and we end up we similar standard values as you. Hence it might not be so important for TDB to add more sophistication in its methodologies, anyhow the SIT formula was chosen to have a reliable way to extrapolate data to I=0, not really to model electrolyte solutions.

However, anion/anion interactions generally become important if the charge of an anion is -2 or larger,
PV 35b
In the case under discussion it is rather the contrary: there is clearly a problem for $NpO_2CO_3^-$ whose activity coefficient indeed seems different in NaCl and NaClO$_4$ media (unless this difference is due to an undetected mixed carbonate chloride complex), while there is no experimental evidence of this difference for the more negatively charged complexes typically K_{s3} ionic strength corrections are the same in both media (see PV 31).

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Page 36
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.
PV 36a
Not really (see discussion above) the solid was possibly slightly changing during then measurement ,and it seems it was not characterised or control after the achievement of equilibrium solubility in ref. [83MAY]

PV 36b

It is not a very good idea to select a correction on the correction of activity, hence a very small difference, from Np(V) carbonate solubility data, because ripening of the solid phase during solubility measurements cannot be ruled out in the existing available experimental information.

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Page 37
PV 37a

The results showed on the figure were essentially discussed above, as was a part of the rest of this Section: more experimental confirmation is needed to check your interpretation.

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Page 38
2.4. Consequences for NEA-TDB reviews

(1) Limitations of the SIT have to be pointed out.
PV 38a

they are already known and documented

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(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
PV 38b

Experimental confirmation is needed

(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.
PV 38c

Only if your interpretation is correct, which needs confirmation

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If possible, the experimental results on H_2CO_3 dissociation constants given in [96FAN/NEC] should be checked in an independent laboratory.
PV 38d

This is the first thing to do, it will then be time for your other proposals if confirmation is obtained

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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.
PV 38e

You will then come into the debate weak complex/activity coefficient to model actinide cations interactions with Cl^-

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(4) Np/Pu review
a) Conclusions for solid Np(V) carbonates are incorrect. The selected log K°_s values have to be changed.
PV 38f

From the above discussion, the qualitative discussion may be reworded, but the problem was handle in our review in a way to limit such systematic deviation, finally the numbers you calculated are usually consistent with the ones calculated in our review. The solid phase problem is quite independent from the activity coefficient discussion: it rely on x-ray studies and kinetics observation, both not much originated from your work.

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b) log β°, and SIT parameters ($\Delta\varepsilon$ and ε) have to be reevaluated, including data in NaCl solution for the equilibria $NpO_2^+ + n\ CO_3^{2-} <=> NpO_2(CO_3)_n^{1-2n}$ (or for the stepwise constants),

because NaCl is an important medium with respect to natural aquatic systems. If necessary, the log $\beta°$ 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±0.02 [95NEC/FAN] and $\varepsilon(Na^+/CO_3^{2-})_{NaCl}$ = -(0.08 ± 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.

PV 38g

Taking data only in NaCl media might end up with taking data only from your laboratory, which is not satisfactory. It seems the solution you propose to avoid this is more or less the same as the one we used in our review; but giving the reverse role to chloride and perchlorate media, I do not thing this is worthwhile to restart all the work this way because of course practically the same standard values would be obtained.

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Page 39

Fig. 2.7

PV 39

These figures might be misleading because it seems that the activity coefficient difference in chloride and perchlorate media is more important for the 1-3 complex than for the 1-2 than for the 1-1, while experimental solubility directly show that there is a difference only for the aquo cation (which is expected) and with the first complex (which is not expected because it is an anion)n using K_{si} better shows this.