Np(V) et Np(VI) en solution aqueuse bicarbonate / carbonate

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Résumé - Les constantes de formation de $NpO_2(CO_3)_i^{1-2i}$ (i = 1, 2 et 3), $NaNpO_2CO_{3(s)}$ et $Na_3NpO_2(CO_3)_{2(s)}$ sont déduites des travaux de Simakin et al. (1977), Maya (1983) et de Vitorge et al. (à partir de 1984) qui ont également montré l'existence d'un complexe mixte (au moins) Np(V)-OH-CO_3. Simakin a mis en évidence $NpO_2(CO_3)_3^{-4}$, ce qui a été confirmés par Riglet (1989) puis Offerlé, Capdevila et Vitorge (1995). L'influence de la température a été mesurée par Ullman et Schreiner (1988), et par Offerlé, Capdevila et Vitorge (1995). Grenthe, Riglet et Vitorge (1986 et 1989) ont mis en évidence $(NpO_2)_3(CO_3)_6^{-6}$. Bien qu'originalement mal interprétés, les travaux de Maya (1984) mettent bien en évidence un complexe mixte polynucléaire, certainement $(NpO_2)_2(OH)_3CO_3^{-1}$. Aucun autre complexe carbonate soluble de Np(V) ou Np(VI) n'est détectable, ceux proposés ici rendent compte quantitativement de l'ensemble des travaux expérimentaux publiés. Quelques données non publiées permettent d'estimer la stabilité des complexes intermédiaires mononucléaires et le produit de solubilité de $NpO_2CO_{3(s)}$. Ceux de $M_4NpO_2(CO_3)_{3(s)}$ ($M^+ = K^+$ ou NH_4^+) sont déduits des mesures de Gorbenko-Germanov et Klimov (1966) et de Moskvin (1975) respectivement interprétées et réinterprétées. Les données thermodynamiques déterminées dans ce rapport sont en cours de discussion au sein de l'OCDE-AEN-TDB.

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Les constantes de formation de $NpO_2(CO_3)_i^{1-2i}$ (i = 1, 2 et 3), $NaNpO_2CO_{3(s)}$ et $Na_3NpO_2(CO_3)_{2(s)}$ sont déduites des travaux de Simakin et al. (1977), Maya (1983) et de Vitorge et al. (à partir de 1984) qui ont également montré l'existence d'un complexe mixte (au moins) Np(V)-OH-CO_3. Simakin a mis en évidence $NpO_2(CO_3)_3^{-4}$, ce qui a été confirmés par Riglet (1989) puis Offerlé, Capdevila et Vitorge (1995). L'influence de la température a été mesurée par Ullman et Schreiner (1988), et par Offerlé, Capdevila et Vitorge (1995). Grenthe, Riglet et Vitorge (1986 et 1989) ont mis en évidence $(NpO_2)_3(CO_3)_6^{-6}$. Bien qu'originalement mal interprétés, les travaux de Maya (1984) mettent bien en évidence un complexe mixte polynucléaire, certainement $(NpO_2)_2(OH)_3CO_3^{-1}$. Aucun autre complexe carbonate soluble de Np(V) ou Np(VI) n'est détectable, ceux proposés ici rendent compte quantitativement de l'ensemble des travaux expérimentaux publiés. Quelques données non publiées permettent d'estimer la stabilité des complexes intermédiaires mononucléaires et le produit de solubilité de $NpO_2CO_{3(s)}$. Ceux de $M_4NpO_2(CO_3)_{3(s)}$ ($M^+ = K^+$ ou NH_4^+) sont déduits des mesures de Gorbenko-Germanov et Klimov (1966) et de Moskvin (1975) respectivement interprétées et réinterprétées. Les données thermodynamiques déterminées dans ce rapport sont en cours de discussion au sein de l'OCDE-AEN-TDB.

Summary

Formation constants for $NpO_2(CO_3)_i^{1-2i}$ (i = 1, 2 and 3), $NaNpO_2CO_{3(s)}$ and $Na_3NpO_2(CO_3)_{2(s)}$ are deduced from Simakin's et al. (1977), Maya's (1983), and Vitorge's et al. data, who also found evidence for a mixed Np(V)-OH-CO_3 soluble complex. Simakin (1977) found $NpO_2(CO_3)_3^{-4}$, it was confirmed by Riglet (1989), and by Offerlé, Capdevila and Vitorge (1995). Temperature influence was studied by Ullman and Schreiner (1988), and by Offerlé, Capdevila and Vitorge (1995). Grenthe, Riglet and Vitorge (1986 and 1989) proved the existence of the trinuclear species $(NpO_2)_3(CO_3)_6^{-6}$. Maya (1984) mis-interpreted his data; nevertheless they show evidence of a new polynuclear mixed species, certainly $(NpO_2)_2(OH)_3CO_3^{-1}$, as initially proposed by Maya. No other Np(V) or Np(VI) soluble complex could be detected, the proposed ones quantitatively account for all published works. Unpublished data allowed to estimate the stability of intermediary mononuclear complexes and $NpO_2CO_{3(s)}$ solubility product. $M_4NpO_2(CO_3)_{3(s)}$ ($M^+ = K^+$ or NH_4^+) ones are deduced from Gorbenko-Germanov and Klimov (1966), and Moskvin (1975) data as respectively interpreted and reinterpreted by this review. Thermodynamic data determined in this report are under discussion within OECD-NEA-TDB.

Sommaire

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Avant-propos

Ce rapport fait suite à la note bibliographique (CEA-BIB-246) sur un sujet voisin : *Neptunium en solution carbonate concentrée réductrice : bibliographie pour l'OCDE-AEN-TDB*. Ces textes pour la banque de données, TDB, sont des contributions au livre à paraître (en 1998 ou 1999) : Lemire R., Fuger J., Nitsche H., Rand M., Spahiu K., Sullivan J., Ullman W., Vitorge P. *Chemical Thermodynamics of Neptunium and Plutonium.* Paris OCDE AEN, Elsevier. Le texte proprement dit des chapitres et de "l'appendix A" sont des versions provisoires, avant adoption par le groupe de travail. Depuis, une réunion finale en décembre 1997 a arrêté la version définitive du livre qu'il est prévu d'envoyer pour une dernière série d'examens externes ("peer review") mi-1998 : les chiffres proposés ici ont très peu varié; par contre le texte lui-même a été raccourci et sa rédaction considérablement améliorée essentiellement en collaboration avec Robert Lemire, président du groupe de travail. Comme le font maintenant la plupart des autres auteurs de ce livre, ces travaux sont pré-publiés (dans ce rapport) pour fournir des détails complémentaires sur la réinterprétation de publications, pour rassembler certains résultats expérimentaux actuellement peu accessibles ou non encore publiés et pour permettre d'éventuels commentaires avant la sortie du livre... tout en limitant l'effet "d'emprunts" des documents et calculs qui circulent dans le cadre de ce travail (dans la thèse [90BEN] sur Pu(V) on retrouve par exemple des photocopies de la thèse [89RIG] de Chantal Riglet sur Np(V) sans la citer ni donner l'information qu'il s'agit de résultats sur Np(V) et non Pu(V)).

Ce rapport est divisé en deux parties indépendantes, l'une sur Np(V), l'autre sur Np(VI). Les données thermodynamiques servent à calculer les concentrations à l'équilibre des espèces solubles susceptibles d'être lixiviées hors d'un stockage éventuel de déchets radioactifs. Trop peu de données expérimentales étaient publiées, et elles comportaient des incohérences. Pour la conception d'un stockage de déchets on utilisera plutôt les données les plus vraisemblables, alors que les données les plus pénalisantes (dont l'absence de données quantitatives) devraient au contraire servir à l'analyse de sûreté. Certaines mesures a priori possibles manquent et il y a beaucoup trop peu de recoupements. La majorité des résultats proposés dans la littérature est peu fiable : soit que la méthodologie expérimentale est imprécise, soit que le traitement des résultats est partiel, voire faux. Il ne suffit donc pas d'effectuer de nouvelles mesures, il faut comprendre les incohérences, corriger les erreurs publiées puis prouver que de nouvelles mesures permettraient effectivement de résoudre les problèmes. Les quelques auteurs ou laboratoires qui ont déterminé des données thermodynamiques correctes, ou au moins qui ont publié des résultats utilisables sur Np(VI) et Np(V) en milieu bicarbonate / carbonate, sont identifiés dans l'introduction de chacune des deux parties, auxquels il faut rajouter, pour Np(IV), Ray et Ryan (1985) pour leurs mesures de solubilité, Fedosseev et Peretrukhin (1979) pour leurs mesures de potentiel d'oxydoréduction et le stage de DEA que Laetitia Delmau [96DEL/VIT] a effectué dans notre laboratoire.

La publication de la série des trois livres de la TDB marque une première étape de synthèse de l'état des connaissances sur la chimie (principalement) en solution aqueuse de l'uranium et des transuraniens, neptunium, plutonium et américium. Même si ce n'est pas toujours explicité dans ces livres, cette synthèse permet de faire le point sur les données manquantes et la façon de les obtenir en tirant des enseignements des erreurs les plus fréquentes à éviter : c'est ce que nous exposons maintenant concernant uniquement les mesures faites dans notre laboratoire, en nous écartant du cadre strict des complexes carbonate pour évoquer également les réactions d'hydrolyse et d'oxydoréduction en milieu non complexant qui interviennent par exemple dans les cycles thermodynamiques les plus précis pour obtenir les données en milieu bicarbonate / carbonate. Les mesures faites au laboratoire l'ont presque toutes été dans le cadre de thèses ou de stage de DEA. Pour une bonne partie, ces travaux visaient à démontrer la faisabilité des mesures, mettre au point la méthodologie, déterminer la précision et vérifier le tout en comparant aux résultats partiels publiés par ailleurs. Bien souvent, il ne reste qu'à les compléter.

Détails expérimentaux

Un des détails qu'il faudrait toujours expliciter est l'**étalonnage de l'électrode de référence** intervenant dans les mesures de pH ou de potentiel d'oxydoréduction. Rappelons qu'il faut travailler à force ionique constante imposée par un électrolyte indifférent de concentration au moins cent fois supérieure à celles des ions étudiés. Quand c'est impossible, on peut alors parfois encore obtenir des résultats assez précis avec quelques approximations bien choisies comme l'ont fait par exemple Hélène Capdevila dans sa thèse [92RIG] et Laetitia Delmau dans son rapport de DEA [96LAE/VIT]. Pour extrapoler à force ionique nulle, il faut au moins une mesure à force ionique 0.5 M et une autre à 3 M (trois mesures intermédiaires sont souhaitables). La base théorique, la plus accessible en français, de cette extrapolation, est la thèse de Chantal Riglet [89RIG]. Travailler à force ionique élevée évite de prendre en compte explicitement les coefficients d'activité qui n'interviennent alors que pour l'extrapolation aux conditions standard, à condition d'étalonner l'électrode de verre en concentration ($-\log_{10}[H^+]$ et non pH). La mesure de pH doit se stabiliser en moins de trente secondes en milieu acide, dont la pente mesurée doit correspondre à la valeur théorique (59,16 mV par unité pH à 25°C) et, comme pour toute mesure, il faut atteindre l'équilibre en le déplaçant dans les deux sens. Si ces vérifications échouent, c'est généralement que l'électrode référence est abîmée (attaquée chimiquement) : il faut la refaire ou la jeter.

Enfin il faut prendre en compte le **potentiel de jonction** entre la solution de travail et celle de l'électrode de référence, on peut le mesurer, le rendre minimal en utilisant des milieux ioniques voisins, Chantal Riglet vient de me faire remarquer qu'il semble préférable d'utiliser des milieux de même force ionique, plutôt que de mêmes concentrations ioniques de part et d'autre de la jonction quand ces deux notions ne sont pas équivalentes.

La **reproductibilité** des constantes d'équilibre d'un laboratoire à l'autre est rarement meilleure que 0.1 unité $\log_{10}$ et plus souvent 0.3 unité $\log_{10}$ correspondant respectivement à 6 et 18 mV. La reproductibilité constatée au laboratoire (sur nos premières expériences qui ont duré plus d'un an, réalisées par Christian Dautel) est de l'ordre de 0.06 unité $\log_{10}$ (4 mV). Les écarts inter-laboratoires proviennent, en fait, au moins aussi souvent d'erreurs systématiques que simplement de différence d'étalonnage. Chercher à améliorer la précision des mesures potentiométriques, ne conduira donc pas forcément à des résultats plus reproductibles. Quelques laboratoires savent réellement obtenir une précision de l'ordre du dixième de millivolt, voire mieux. Pour les mesures d'oxydoréduction, nous estimons en général à 5 mV l'incertitude d'une mesure ;

mais l'erreur statistique de certains résultats de la thèse d'Hélène Capdevila [92CAP] est de l'ordre de 1 mV. L'influence de la température sur les constantes d'équilibre, est généralement faible, parfois à peine supérieure à l'incertitude, ou inférieure aux corrections de force ionique. Il faut recommencer les étalonnages à chaque température, en particulier remesurer le potentiel de jonction à chaque température et force ionique. On voit donc l'intérêt qu'il y a, chaque fois que c'est possible, à utiliser le même milieu ionique de part et d'autre de la jonction.

Ions aqueux

Les potentiels d'**oxydoréduction des couples réversibles** de U, Np, Pu ont été mesurés au laboratoire par voltampérométrie cyclique au cours des thèses de Piotr Robouch (1987), Chantal Riglet et Hélène Capdevila, confirmant des mesures existantes et les complétant, ne serait ce que pour l'extrapolation à force ionique nulle. L'influence de la température n'a été qu'esquissée [92CAP], il faut la prolonger sur l'uranium et le neptunium (au moins) en mesurant le potentiel de jonction à toute force ionique et température. Il faudrait aussi déterminer la correction due à la différence entre les coefficients de diffusion des espèces électroactives [89RIG] à toute température et force ionique : voir si on peut déduire cette correction de l'influence de la vitesse de balayage sur les potentiels de pic.

Pour les potentiels des **couples irréversibles**, les mesures sur le plutonium sont particulièrement délicates du fait des dismutations de Pu^{4+} et de PuO_2^+, à moins justement d'étudier (il y a eu environ un an de mesures) ces équilibres [92CAP] sur lesquels il faut maintenant étudier l'influence de la température, si possible en couplant potentiométrie et spectrophotométrie. Pour le neptunium il n'y a qu'une seule valeur publiée, il faut donc la vérifier, étudier l'influence de la température et de la force ionique par potentiométrie statique (voir la méthodologie utilisée en milieu complexant [96DEL/VIT]) ; mais cette méthode est relativement délicate et peu rapide. On pourrait essayer d'utiliser des électrolyses partielles dans une électrode à pâte de carbone, technique à mettre au point et à nucléariser pour ce type de mesures.

Les **coefficients d'activité** des ions non complexés, se déduisent classiquement de mesures isopiestiques ; mais ces mesures n'ont pas été faites pas pour les transuraniens. D'un autre coté elles mettent en oeuvre des quantités importantes de radioéléments, et l'interprétation peut être perturbée par la radiolyse, voire l'hydrolyse et même la dismutation. Des résultats équivalents peuvent en principe être obtenus à partir de mesures de solubilité, à condition d'obtenir une phase solide bien cristallisée et en équilibre avec les solutions aqueuses.

Complexes limite carbonate

Les complexes limite carbonate des actinides sont tous anioniques et de stabilités suffisantes pour préparer ces éléments à des concentrations élevées. On a ainsi des solutions mères en milieu alcalin, point de départ préférable pour toutes les études en milieu non-acide afin d'éviter les réactions peu réversibles d'hydrolyse (comme signalée ci-dessous pour les actinides au degré d'oxydation quatre, par exemple). De nombreuses méthodes physiques de mesure peuvent leur être alors appliquées. Les équilibres d'oxydoréduction sont utilisés dans les cycles thermodynamiques notamment pour obtenir des données sur les actinides au degré d'oxydation quatre, peu solubles, à partir de leurs formes oxydées, plus solubles.

Le contrôle des conditions chimiques en milieu carbonate, suppose de maîtriser deux paramètres (et non uniquement le pH) et de les faire varier indépendamment pour déterminer la stoechiométrie des équilibres étudiés [87ROB]. Il faut naturellement travailler en milieu tampon, pratiquement avoir des concentrations au moins égales à 0,1 mM (et plutôt 1 mM) pour chacun des éléments du couple OH^-/CO_3^{2-}, CO_3^{2-}/HCO_3^- ou $HCO_3^-/CO_{2(gaz)}$. Il faut éviter de passer directement d'une solution acide de Pu^{4+} (et vraisemblablement des autres ions actinides et lanthanides^{4+}) en milieu alcalin (y compris bicarbonate ou carbonate) car des quantités incontrôlables d'hydroxyde se forment de façon quasi irréversible.

Les potentiels d'**oxydoréduction des couples réversibles** de U, Np et Pu ont été mesurés par voltampérométrie cyclique [89RIG, 92CAP, 95OFF/CAP] en fonction de la température et de la force ionique. Comme en milieu non complexant, des mesures complémentaires seraient utiles.

Pour les potentiels des **couples irréversibles**, des mesures par potentiométrie statique ont été mises au point en stage par Laetitia Delmau [96DEL/VIT] et Christine Poulangy [92CAP] ce qui permet de déduire la stabilité des complexes de Np(IV) et Pu(IV), qui, pour ce dernier, peut également être déduite du suivi spectrophotométrique de la dismutation de Pu(V) comme l'a montré Eric Giffaut lors de son stage de DEA [92CAP]. Il faudrait maintenant appliquer systématiquement ces méthodes (en couplant spectrophotométrie et potentiométrie). C'est une priorité à la fois pour l'importance pratique de la chimie des actinides en milieu réducteur (correspondant aux eaux souterraines), parce que la stoechiométrie des complexes limite n'est pas vraiment démontrée et parce que leur stabilité n'est pas connue avec une précision suffisante.

Jacques Bourges [83BOU/GUI] a montré et étudié par voltampérométrie cyclique la stabilité de l'**américium** sous quatre degrés d'oxydation en milieu bicarbonate / carbonate concentré. Il faudrait reproduire ces mesures en fonction de la température et de la force ionique, en mesurant le potentiel de jonction et en essayant d'atteindre l'équilibre pour des couples irréversibles. Comme des mesures équivalentes en milieu non complexant sont impossibles, les constantes de complexation pourraient être estimées à partir de celles, en milieu carbonate, interprétées par analogie avec les complexes limite des autres actinides. Cela suppose de mieux comprendre les variations systématiques au sein de la série des actinides. On s'attend, surtout pour les complexes limite, à ce qu'elles soient principalement gouvernées, pour les ions analogues, par le rayon ionique. Des mesures systématiques d'**EXAFS** seraient donc utiles pour obtenir ces paramètres géométriques. David Clark (Los Alamos) s'est fait une spécialité de ce type de mesures à partir de nos publications (donnant les conditions exactes de préparation des complexes) ; mais il existe des installations en France (LURE à Orsay et semble-t-il à Grenoble). L'américium, comme le **cérium** au degré d'oxydation quatre, se prêtent à l'étude par voltampérométrie où chaque mesure est relativement rapide. Des premiers essais sur le couple Ce(IV)/Ce(III) sont en cours (Riglet, Vitorge, Calmon à la conférence Migration 97).

Complexes carbonate intermédiaires

L'ajout de ligand (carbonate) conduit généralement à la formation d'un complexe avec un ligand, puis deux et ainsi de suite jusqu'au complexe limite. Cette règle n'est pas absolue. Dans le cas des ions (dits durs) des séries f dont la chimie est gouvernée par des liaisons à caractère principalement électrostatique, l'ajout (en fait l'échange avec une ou es molécules d'eau) de chaque nouveau ligand électronégatif se fait sur une entité de moins en moins électropositive et de plus en plus encombrée stériquement ce qui explique que les domaines de stabilité des complexes traduisent bien l'ajout des ligands un par un.

La stabilité des complexes soluble (dont les complexes limite donc) a été étudiée directement par **solubilité** pour l'américium [87ROB, 94GIF], Np(V) et Pu(VI) [87ROB]. Par principe cette méthode ne permet pas (mathématiquement) de déterminer la stoechiométrie de complexes polynucléaires, sauf si on peut utiliser plusieurs phases solides dans des conditions chimiques appropriées. Le solide en équilibre avec la solution n'est pas forcément celui introduit initialement (il faut donc le caractériser en fin d'expérience par son spectre de diffraction de rayons X), ni même parfois celui le plus visible (sur un spectre de diffraction de rayons X). Le temps pour obtenir l'équilibre est très variable d'un composé à l'autre, il faut donc si possible mesurer la solubilité par dissolution et précipitation. L'augmentation de la température pourrait en principe accélérer la mise à l'équilibre et permettrait d'obtenir des phases mieux cristallisées. Toutefois pour Am(III) et Np(V) ces avantages sont compensés par des changements de stoechiométrie, de structure ou du nombre de molécules d'eau. La radiolyse dans le solide $PuO_2CO_{3(s)}$, conduit à la réduction de Pu(VI) en Pu(IV). Malgré toutes ces difficultés, il serait utile de disposer de plus de résultats expérimentaux en fonction de la température et de la force ionique sur la solubilité des phases déjà étudiées ou en substituant dans certaines d'entre elles Na^+ par d'autres cations, généralement plus gros, pour obtenir des phases plus stables et mieux cristallisées. On détermine ainsi la stabilité des complexes à partir forcément de phases solides bien caractérisées, ce qui n'est pas toujours le cas de celles qui limiteraient la solubilité de radioéléments en milieu naturel ou perturbé. Le curium teste à étudier.

La **spectrophotométrie** classique d'absorption UV / visible / Proche InfraRouge a permis d'obtenir des résultats sur Np(V) [89RIG] et la dissociation de complexes limite [92CAP, 96DEL/VIT] ; mais on est souvent gêné par la faible solubilité des actinides dans les conditions chimiques où se forment les complexes intermédiaires. Ce problème peut être évité pour Np(V) en substituant Na^+ de l'électrolyte, par un autre cation, au prix d'obtenir les données auxiliaires sur le nouvel électrolyte. Sinon il faut employer des techniques plus sensibles utilisant des lasers ; mais, comme il ne s'agit pas d'appareillage de routine, il faut collaborer avec les équipes mettant au point ces dispositifs pour valider les données thermodynamiques déduites de ce type de mesure (comme nous l'avions fait avec d'autres techniques plus classiques). L'interprétation des résultats est très difficile quand plusieurs complexes intermédiaires coexistent, sans qu'il soit possible de les préparer pur chacun ; mais on devrait pouvoir améliorer le traitement en décomposant les spectres comme l'a fait Christine Cuillerdier dans sa thèse (1980). Les mesures spectrophotométriques qu'il reste à faire concerne l'influence de la température sur les équilibres déjà étudiés et la recherche systématique de complexes mixtes par ajout de OH^- aux complexes limite.

Hydrolyse

Des mesures spectrophotométrique devraient permettre d'améliorer les connaissances sur l'hydrolyse de Pu(VI), Np(V) et sans doute Np(VI). L'hydrolyse des actinides au degré d'oxydation six s'accompagne de polymérisation, semble-t-il assez lente. Il faut donc étudier l'influence de la concentration totale en métal et faire varier le pH dans les deux sens. La complexation par les carbonates (due au gaz carbonique de l'air) est certainement gênante pour l'étude de l'hydrolyse de Np(V), travailler en présence de $Ba(OH)_{2(s)}$ directement dans la solution pourrait être une solution pour éviter cette interférence.

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Np(V) en milieu bicarbonate / carbonate

Pierre Vitorge

Résumé

Les constantes de formation des complexes solubles $NpO_2(CO_3)_i^{1-2i}$ (i = 1, 2 et 3) et des solides $NaNpO_2CO_{3(s)}$ et $Na_3NpO_2(CO_3)_{2(s)}$ sont déduites des travaux originaux rigoureux de Simakin et al. (1977) et Maya (1983) complétés par la série de mesures de Vitorge et al. (à partir de 1984) qui ont également montré l'existence d'un complexe mixte (au moins) Np(V)-OH-CO_3. Les nombreuses publications ultérieures, de Kim et al. par exemple, confirment les précédentes en ajoutant toutefois une certaine confusion due à des imprécisions ou erreurs méthodologiques notamment à force ionique élevée. Les coefficients d'activité des espèces solubles sont déterminés selon la TIS. Aucun autre complexe carbonate soluble de Np(V) n'est détectable, ceux proposés rendent compte quantitativement de l'ensemble des travaux expérimentaux publiés. Les résultats disponibles ne fournissent que des indications parcellaires de l'influence de la température et de la stabilité de solides de K^+ et NH_4^+ analogues à ceux de Na^+. La précision des données thermodynamiques est limitée par l'incertitude sur celles concernant $NpO_2CO_3^-$. On pourrait améliorer cet ensemble en développant les mesures spectrophotométriques préliminaires de Clark et al. (1996) à condition d'y appliquer la rigueur méthodologique de Riglet (1989).

Summary

Formation constants for $NpO_2(CO_3)_i^{1-2i}$ (i = 1, 2 et 3) soluble complexes, and $NaNpO_2CO_{3(s)}$ and $Na_3NpO_2(CO_3)_{2(s)}$ solid compounds are deduced from reliable works by Simakin et al. (1977) and by Maya (1983), also using Vitorge's et al. data, who also found evidence for a mixed Np(V)-OH-CO_3 soluble complex. Later publications typically from Kim et al., were consistent with these first ones; but added confusing numbers due to inaccuracy or incorrect methodology typically at high ionic strength. Activity coefficients were proposed according to the SIT formula. No other Np(V) soluble complex could be detected, the proposed ones quantitatively account for all published works. Available data can only give rough estimates for temperature influence and for K^+ and NH_4^+ solid compounds analogue of Na^+ ones. Precision on the proposed thermodynamic data is limited by the uncertainty on $NpO_2CO_3^-$ data. It could be improved by developing Clark et al. (1996) preliminary spectrophotometric measurements, but using Riglet's (1989) accurate methodology.

Sommaire

Introduction

Cette note bibliographique fait suit à une précédente (CEA-BIB-246) sur un sujet voisin : « Neptunium en solution carbonate concentrée réductrice : bibliographie pour l'OCDE-AEN-TDB ». Toutes deux, ainsi qu'une troisième (sur Np(VI)) en cours de relecture, sont destinées à faire partie du livre à paraître (vraisemblablement en 1998) : Lemire R., Fuger J., Nitsche H., Rand M., Spahiu K., Sullivan J., Ullman W., Vitorge P. *Chemical Thermodynamics of Neptunium and Plutonium* Paris OCDE AEN. Deux volumes précédents sur l'uranium et l'américium sont déjà parus. Une dernière séance de travail devra nous permettre de mettre un point final à cet ouvrage, avant de le faire examiner par des experts extérieurs (peer review). Les résultats présentés ici ne sont donc en principe pas définitifs. J'ai décidé de pré-publier ces travaux sous forme de note CEA-BIB notamment pour fournir des détails complémentaires sur la réinterprétation de publications, pour rassembler certains de nos résultats expérimentaux actuellement peu accessibles ou non encore publiés et pour permettre d'éventuels commentaires avant la sortie du livre.

Comme l'observation de propriétés chimiques dans des « conditions représentatives » (d'un stockage de déchets ou son environnement naturel par exemple) ne permet généralement pas de déterminer les données (stoechiométrie, stabilité thermodynamique en premier lieu) nécessaire aux extrapolations (du comportement dans le temps et l'espace), on doit étudier la chimie des radioéléments dans des conditions contrôlée, propices à mettre en évidence chaque espèce chimique pour ensuite mesurer les données nécessaires. Parmi les actinides au degré d'oxydation cinq, seul Np(V) est suffisamment stable chimiquement pour se prêter aux mesures nécessaires à l'obtention de données fiables. L'uranium et les transuraniens au degré d'oxydation cinq, présentent des propriétés chimiques particulières, qu'il est pratiquement impossible d'étudier en solution aqueuse sur des éléments (ou analogues) non radioactifs. Les données sur Np(V) sont donc particulièrement importantes. Par analogie elles servent également de référence pour comprendre le comportement notamment du plutonium dans certaines conditions.

Trois laboratoires (Simakin, Maya et le notre) ont produit en 1977-1989 l'essentiel des mesures sur lesquelles s'appuyer pour extraire des données thermodynamiques rendant compte essentiellement de la chimie de Np(V) en solution aqueuse bicarbonate / carbonate. Ceux sont vraisemblablement les seuls travaux publiés sur le sujet ne comportant pas de biais d'étalonnage. Par la suite ces travaux ont été reproduits et confirmés par l'équipe de Kim (Munich) ; mais nous avons relevé quelques incohérences internes des données numériques publiées, ainsi qu'un étalonnage douteux, ce qui finalement conduit à augmenter l'incertitude malgré le volume relativement important de publications produites. Contrairement à l'impression que cette équipe veut donner, il n'y avait pas accord quantitatif entre les divers résultats de mesure de solubilité et lorsqu'on compare ces derniers à ceux issus de mesures spectrophotométriques (même si on corrige les erreurs évoquées plus haut). Ces écarts de solubilité s'expliquent par la difficulté à préparer des phases solides de façon reproductible ce qui est connu depuis mes travaux (1984) et surtout ceux de Lemire (AECL Canada) en 1993. Le traitement des résultats de mesures spectrophotométriques nécessite d'obtenir par le calcul les coefficients d'extinction molaire des complexes $NpO_2CO_3^-$ et $NpO_2(CO_3)_2^{-3}$ (leur mesure directe n'est pas possible) ce qui suffit à expliquer les difficultés d'interprétation (thèse de Riglet préparée sous ma direction en 1989). Le travail pour l'OCDE-AEN-TDB permet de faire le tri entre les données existantes et propose finalement un ensemble de données cohérentes. Ainsi, depuis le début des années 1980 on connaît l'essentiel des données numériques sur la chimie de Np(V) en solution aqueuse bicarbonate / carbonate qui interviennent (avec d'autres) pour prévoir (modéliser) son comportement dans l'environnement. La précision nécessaire pour ce type d'évaluation est en effet suffisamment peu contraignante. Par contre une plus grande précision est nécessaire pour des études démonstratives de la maîtrise du couplage du transport avec (entre autres) les réactions chimiques en solution aqueuse et naturellement pour utiliser les résultats dans des cycles thermodynamiques ou les inclure dans une base de données. Pratiquement rien n'est connu sur l'influence de la température par exemple.

Après quelques observations qualitatives d'Alain Billon [81BIL], l'étude de la solubilité [84VIT, 85COM, 85KIM, 86GRE/ROB] puis des spectres d'absorption proche infrarouge / visible [89RIG] de Np(V) en milieu bicarbonate / carbonate est la première contribution du CEA à la chimie des transuraniens dans le cadre du développement (international) de l'effort de recherche sur les bases scientifiques pour la gestion et le stockage éventuel de déchets radioactifs. Nous avons bénéficié au départ de l'impulsion donné par Guy Baudin (chef de service puis de département au CEA) qui a permis une réelle collaboration avec Ingmar Grenthe (Stockholm). C'est lui qui nous a donné l'idée initiale de mesurer la solubilité de $NaNpO_2CO_{3(s)}$, il est venu avec Diego Ferri nous aider à démarrer les mesures réalisées par Christian Dautel (dont les résultats peu accessibles jusqu'à présent, sont réunis pages 49 à 58), puis par la suite Ingmar Grenthe a passé un an avec moi au laboratoire. Ce travail a également fait l'objet dans les années 1980, de contrats européens (CCE) généralement dirigés par Kim ; qui se chargeait de fondre en un rapport unique les résultats des différents laboratoires en en gommant les écarts.

Ingmar Grenthe a été le responsable du premier groupe de travail de la TDB (sur l'uranium) auquel il a donné l'essentiel de ses méthodologies : il s'agissait surtout de faire le tri entre une multitude de données en se basant essentiellement sur la réinterprétation des mesures publiées. Le travail sur le neptunium (et le plutonium qui est mené au sein du même groupe de la TDB) s'appuie par contre sur beaucoup moins (trop peu) de données publiées, on a donc essayé de tirer des interprétations quantitatives de tout ce qui est disponible, y compris de travaux (malheureusement les plus nombreux) de qualité insuffisante, en traduisant les problèmes rencontrés dans l'évaluation des incertitudes.

The aqueous neptunium-hydroxide-carbonate-bicarbonate system.

Np(V) carbonate and mixed hydroxide-carbonate complexes

Np(V) carbonate chemistry has been studied quite recently. Nigon, Penneman, Staritzky et al. reported $KNpO_2CO_{3(s)}$ precipitation from a potassium carbonate aqueous solution [54NIG/PEN]. Keenan and Kruse later characterised this compound by its X-ray diffraction pattern [64KEE/KRU]. Gorbenko-Germanov and Zenkova [66GOR/ZEN] prepared the same hydrated compound, and the $K_3NpO_2(CO_3)_{2(s)}$ one. Volkov et al. later proposed structures for these types of compounds for Np(V), Pu(V) and Am(V), where K^+ could be exchanged for other alkaline cations or for the NH_4^+ or possibly divalent ones; but in this series of publication (starting by the [74VIS/VOL] one and finishing with the [81VOL/VIS4] one) some propositions need confirmations (see the appendix A).

Gorbenko-Germanov and Zenkova [66GOR/ZEN] also published absorption spectra of their aqueous solutions, that were later confirmed [75UEN/SAI] and identified [89RIG] to be an evidence of the limiting complex $NpO_2(CO_3)_3^{5-}$. Simakin [77SIM] deduced the correct stoichiometry of this limiting Np(V) carbonate complex, from solubility measurements of a hydrated $Na_3NpO_2(CO_3)_{2(s)}$ compound at constant ionic strength (3 M $NaNO_3$) in concentrated carbonate aqueous solutions. The full demonstration of this stoichiometry was only confirmed later (see the discussion of the [77SIM] publication and of Riglet's thesis [89RIG] in the appendix A). Simakin's measurements were the first reliable work from which this review could deduce a thermodynamic constant.

Billon [81BIL] showed evidence of the formation of soluble complexes. It was a preliminary work that was later continue in the same laboratory by Vitorge [84VIT], Riglet [89RIG] and in collaboration with Grenthe [86GRE/ROB] and within the framework of European collaboration with Bidoglio who used liquid-liquid extraction technique [85BID/TAN], and with Kim who wrote summarised report [85COM and 85Kim]. Billon's spectrophotometric observations can be explained with the formation of the $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{2-}$ intermediary complexes after Riglet's thesis, and this European collaboration produced contradictory formation constant for these intermediary complexes. Meanwhile Maya deduced the Np(V) carbonate complexing constants from the solubility study of a hydrated $NaNpO_2CO_{3(s)}$ compound. Maya's work is one of the basis of the thermodynamic data selection by this review.

Varlashkin, Begun and Hobart reported [84VAR/BEG] Np(V) spectral variations when adding NaOH to concentrated Np(V) carbonate aqueous solutions. This was later confirmed by Riglet [89RIG] and interpreted as an evidence of the formation of mixed Np(V) hydroxide-carbonate complexes.

In here thesis, Riglet used various Np(V) concentrations, solubility and spectrophotometric techniques and she varied independently the speciation parameters of the aqueous carbonic / bicarbonate / carbonate / hydroxide system in a sufficiently large chemical domain to confirm or demonstrate previous assumptions made in the above works: beside this mixed hydroxide-carbonate complex only formed in concentrated hydroxide-carbonate media, the Np(V) complexes in carbonic / bicarbonate / carbonate aqueous solutions are mononuclear, and contain only the carbonate ligand: they are $NpO_2(CO_3)_i^{1-2i}$ (i = 1, 2 and 3).

Most of the useful work to select thermodynamic data was then published, and this review prepared a first drat of this chapter to propose complexing constants extrapolated to zero ionic strength, based on Maya's [83MAY] and Vitorge's et al. [84VIT, 85COM, 85KIM 86GRE/ROB and 89RIG] solubility measurements in 1 and 3 M $NaClO_4$ media, and to a less extend on Riglet's spectrophotometic study [89RIG], and on the liquid-liquid extraction results of Bidoglio, Tanet and Chatt, and of Inoue and Tochiyama [85INO/TOC]. This first draft was not published; but most of his results appeared in some of the reports and publications cited above. The two [83MAY and 86GRE/ROB] solubility works seemed to be the most reliable ones, the extrapolation to zero ionic strength of the stepwise formation constants determined in these two works was then systematically compared to the selection made by this review, that also includes other results (see below). Still, Maya and Vitorge probably did not use the same solid phases (see the discussion of the [83MAY, 84VIT and 89RIG] publications in the appendix A); but the corresponding systematic error was minimised by using stepwise formation constants. Anyhow this problem in the solid phase is now better understood (see below and the discussion of the hydrated $NaNpO_2CO_{3(s)}$ solubility product). Then, even in the most reliable studies, there are still some problems, and there is then still a doubt on he selection of the Np(V) thermodynamic data proposed (below) by the present review, on the $NpO_2CO_3^-$ formation constant and specially on the ionic strength corrections used (namely the value of the $\varepsilon(Na^+,NpO_2CO_3^-)$ specific interaction coefficient determined in the present review). This doubt propagates on the formation constants and specific interaction coefficients for the other carbonate complexes, since stepwise complexing constants had to be used. New reliable experimental measurements are then still wanted, and it seems possible to obtain the needed information following Riglet [89RIG] and Clark et al. [96CLA/CON2] spectrophotometric methodology (some indications are given below). Unfortunately the publications that appeared after the above work only added confirmation; but not better accuracy (as expected when increasing the number of experimental determinations without systematic error, specially correct calibration).

Nitsche, Standifer and Silva [90NIT/STA] and Kim or his co-authors [91KIM/KLE, 94MEI, 94NEC/KIM, 94NEC/RUN, 95FAN/NEC, 95NEC/FAN, 95NEC/RUN, 96FAN/NEC and 96RUN/NEU] recently reproduced Vitorge's measurements at different ionic strengths in Na^+, (ClO_4^- or Cl^-) media, and proposed complexing constant values extrapolated to zero ionic strengths; but these extrapolations were not considered by this review because no difference could be made between ionic strength corrections (namely fitted specific interaction coefficients, ε) and systematic errors in the literature data used for these extrapolation, often due to incorrect pH calibration, and, for solubility measurements, chemical evolution of the solid phases used. Kim and his co-authors made an effort to explain and check their pH calibration procedure; but, beside the problems in the solid phases, this review possibly did not completely understand their calibration, and found inconsistency with well-known published data, and even between the own publications of this group of co-authors (see the discussion of the [91KIM/KLE] report in the appendix A). Hopefully these inconsistencies cancelled at low ionic strength, so among the equilibrium constant values proposed by Kim (or re-evaluated by this review from his experimental data) this review finally used only the ones extrapolated to zero ionic strength from his experimental data measured by this group of authors. This was done for most the authors: none or only one value was used from each laboratory, for proposing selected thermodynamic data. This avoided to give too much weight to possible systematic error or deviation, since all the published data had some.

Several experimental observations on Np(V) in bicarbonate or carbonate aqueous solution, were also published [71MOS5, 75UEN/SAI, 79MOS/POZ and 81BIL]. They could not be used to propose selected thermodynamic data; but it was shown (in the appendix A), that no new species was needed to understand these experimental observations: in contradiction with what Moskvin claimed, no evidence of the $NpO_2HCO_{3(aq)}$ [63MOS/GEL], or $NpO_2OHCO_3^{-2}$ or $NpO_2OH(CO_3)_2^{-4}$ [71MOS5] species was found (see the appendix A). He proposed this new species, only because the interpretations of his experimental observations were completely erroneous.

Lemire, Boyer and Campbell studied the temperature influence on Np(V) solubility. They found that their results seemed to be in contradiction with Visyashcheva, Volkov, Simakin et al. observation [74VIS/VOL], and that they were difficult to interpret; for this reason, they did not publish their preliminary results shown in the Migration 87 conference [87LEM/BOY]; and tried to obtain more reproducible solubility. They finally published these data recently [93LEM/BOY], they qualitatively confirm that there are problems in solid phases that are explained below (when selecting solubility products of hydrated $NaNpO_2CO_{3(s)}$ and $Na_3NpO_2(CO_3)_{2(s)}$ compounds). Clark, Conradson, Ekberg et al. [96CLA/CON2] reported temperature influence results that also seemed to be in contradiction with Lemire's observation. This review estimated that all these results mainly show that the variations of the Np(V) carbonate complexing constants with temperature, are probably less than the actual accuracy of their determination at each temperature, and that no data can be extracted for the solid compounds.

Most of the complexing constant determinations used solubility measurements. Solubility was then typically controlled by the

$$NaNpO_2CO_{3(s)}.xH_2O + (i - 1)\ CO_3^{-2} \Leftrightarrow Na^+ + NpO_2(CO_3)_i^{1-2i} + x\ H_2O$$

equilibria (i = 1, 2 and 3). This interpretation assumes that no Np(V) carbonate polynuclear or mixed complexes were formed. Only Riglet et al. cared for this problem and clearly demonstrated this assumption [86GRE/ROB and 89RIG]. The treatment of the data (typically curve fitting) is equivalent to slope analysis of the log(solubility) vs. $\log[CO_3^{-2}]$ that gives the possible (i - 1) integer values, and the corresponding equilibrium constant, $K_{s1,i} = K_{s1}\ \beta_i$. The classical K_{s1} and β_i values are then deduced from thermodynamic cycle. As discussed below (when selected solubility products) and in the appendix A (see the discussion of the [84VIT, 89RIG and 93LEM/BOY] publications) well characterised hydrated solid phase was difficult to obtain, it was possibly changing during solubility measurements, it was always metastable in conditions where at least $NpO_2(CO_3)_3^{5-}$ was formed. These kinetic problems could also vary within the same set of measurements by the same author. To avoid this problem, this review used another set of equilibria to interpret solubility measurements. One of them corresponds to the solubility product (i = 0) and its determination was then dependent on these kinetic problems, while the author equilibria

$$NpO_2(CO_3)_{i-1}^{3-2i} + CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_i^{1-2i}$$

correspond to the stepwise complexing constants, $k_i = \beta_i / \beta_{i-1} = K_{s1,i} / K_{s1,i-1}$, and are not directly dependent on the solid phase problem. These stepwise constants were also directly measured when using absorption spectrophotometry or liquid-liquid extraction techniques.

Several papers appeared recently were extrapolations to zero ionic strength were proposed [94NEC/RUN, 94NOV/ROB, 95FAN/NEC, 95NEC/RUN and 96RUN/NEU], by using the SIT or Pitzer equations. The problem is not in the choice of the empirical activity coefficient formula; but in the consistency of the thermodynamic approach and in fitting too many and too correlated parameters, that can lose there chemical or physical meaning for this reason. To avoid this last problem it was typically proposed [95FAN/NEC] to use empirical correlation between Pitzer parameters for monocharged species. In this way, this review checked that approximations equivalent to the SIT ones could be used with many sets of Pitzer parameters (i.e. considering only the published pair interaction parameters for ion with opposite charges and neglecting -setting to zero- all the other Pitzer parameters). Unfortunately this could be done with all the Pitzer parameters proposed in this publication (see the discussion of the [96RUN/NEU] publication in the appendix A); except with the Pitzer parameters for Np(V) carbonate complexes [94NOV/ROB, 95FAN/NEC and 96RUN/NEU], possibly because the proposed Pitzer interaction parameters for species with the same charge should not be neglected, the mathematical formula is still correct while the physical meaning of these parameters is no more justified which might explain why the above approximation is no more possible for this particular set of Pitzer parameters. Possible calibration deviation, that increased with ionic strength was also suspected in some of this series of publication (see the appendix A), so these problems should be solved prior to any extrapolation to zero ionic strength, otherwise this error is propagated on the activity coefficient fitted parameters (whatever their are: SIT or Pitzer ones).

a) Np(V) carbonate complexes

As indicated above, there are problems in the interpretation of solubility data, these problems are not much discussed in the present paragraph on the selection of formation constants for aqueous carbonate complexes: they are rather discussed when selecting alkali-Np(V)-carbonate solubility products (below).

The equilibrium constants,
$k_1 = \beta_1$, for $NpO_2^+ + CO_3^{-2} \Leftrightarrow NpO_2CO_3^-$
and $k_2 = \beta_2 / \beta_1$, for $NpO_2CO_3^- + CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_2^{-3}$

were measured by Bidoglio, Tanet and Chatt using a liquid-liquid extraction technique with a 0.1 or 0.2 M $NaClO_4$ aqueous solution [85BID/TAN]. Their β_1 value did not correspond do the experimental data shown on figures of the publication; it was then re-evaluated by this review (see the appendix A). Anyhow none of these β_1 values, neither the k_2 one, are in accord with other published works and with the thermodynamic data proposed by this review. This was possibly due to unrecognised side reaction in the liquid-liquid system. These data were then not considered.

Inoue and Tochiyama also used a liquid-liquid extraction technique to determine β_1 and β_2 values in 1 M $NaClO_4$ aqueous solution [85INO/TOC]. The β_1 and k_2 determinations are neither in accord with the thermodynamic data proposed by this review within the very small uncertainty they estimated. This good statistical accuracy was check by this review; but uncertainty was increased because there was not enough information on pH calibration (see the appendix A). The new (less accurate) values are now consistent with published data and with the value selected by this review. Still this work was not used by this review to propose thermodynamic data.

β_1, k_2 and the stepwise complexing constant
$k_3 = \beta_3 / \beta_2$, for $NpO_2(CO_3)_2^{-3} + CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_3^{-5}$
can be deduced from absorption spectrophotometric study (see the discussion of the [89RIG] thesis in the appendix A); but it is much more difficult for k_2, because the $NpO_2CO_3^-$ complex cannot be obtained alone to measure its molar absorptivity. This difficulty is even more important at high ionic strength. This in turn induces difficulties when treating the experimental data to obtain β_1 and k_3 values. Too low solubility can also be a problem for β_1 and k_2 determinations.

In here thesis, Riglet used this technique to measure the three stepwise constants k_1, k_2 and k_3; and she showed that there are some difficulties to interpret accurately all the results, because it was difficult to obtain k_2. She pointed out that this difficulty cancelled, for ionic strength correction, and the present review followed here specially for k_3. Riglet's β_1 values in 0, 0.5, 1 and 2 M $NaClO_4$ aqueous solutions are in accord with published ones within uncertainties; they are lower than the values selected by this review (but still in accord within uncertainty). The corresponding $\Delta\varepsilon_1$ is in fair agreement with the one selected by this review (see the table). This review could only redetermine the β_1 value in 0.5 M $NaClO_4$ aqueous solutions from the experimental information available in this thesis (see the discussion of the [89RIG] thesis in the appendix A). Only this value (at I = 0.5 M) was used among the Riglet's β_1 spectrophotometric data, to calculate the $\beta_1°$ value proposed by the present review.

Her k_2 values in 0, 0.5, 1 and 2 M $NaClO_4$ aqueous solutions are not in accord with published ones within the 0.07 $\log_{10}$ unit uncertainty reported by the author; but this (very small) uncertainty was increased by this review to account for the difficulty in the interpretation of such data (as explained above). These k_2 data were then in accord with those selected by the present review. The extrapolation to zero ionic strength (by using the SIT) of Riglet's spectrophotometric data, gave $\log_{10}k_2$ and the corresponding $\Delta\varepsilon_2$ values in reasonable agreement with those proposed by the present review; but non of Riglet's k_2 values was used because the experimental information available in here thesis was not enough to allow k_2 redetermination.

There is the same (relatively small) disagreement between the (too accurate) k_3 data proposed by Riglet and the thermodynamic constants selected by this review; but this review could redetermine them (see the appendix A) by using spectrophotometric results that showed the carbonate concentration where no more than about 25 % of the limiting complex was dissociated. This minimised the systematic error due to the second dissociation. These redeterminations are in fair agreement with the thermodynamic data selected by this review. Riglet's k_3 values in 0, 0.5, 1 and 2 M $NaClO_4$ and 0.17 M Na_2CO_3 aqueous solutions, as redetermined by this review were extrapolated to zero ionic strength (by using the SIT); which gave $\log_{10}k_3$ and the corresponding $\Delta\varepsilon_3$ values in accord with those proposed by the present review. Only the value at zero ionic strength was used by this review to calculate selected thermodynamic data, to avoid giving too much weight to a single laboratory (as explained above, here the problem is the difficulty in the treatment of the data). The ionic strength effect was still taken into account in this selection, because another data [86GRE/ROB] from the same laboratory (Vitorge's), obtained at high ionic strength (3M) was also used (see below). Riglet's data also indicate that the SIT is still a reasonable approximation up to at least I = 3M ($NaClO_4$) for the Np(V) carbonate equilibria, even for those with the highly negatively charged (-5) limiting complex.

Nitsche, Standifer and Silva [90NIT/STA] reproduced Riglet's experiments in 0.1 M $NaClO_4$ aqueous solution. The value they found was in accord with some published works; but not with the value selected by this review. Still it seems that there were errors in the treatment of the experimental data (see the appendix A), and this review re-evaluated the β_1 value from the experimental information available in the [90NIT/STA] publication (see the appendix A). The value then found was in perfect agreement with the data proposed by this review. This review also increased the uncertainties for possible systematic errors as reflected by the interpretation of the experimental data, and used this [90NIT/STA] publication to select β_1 data at zero ionic strength.

Nitsche, Standifer and Silva [90NIT/STA] extrapolated published data to zero ionic strength by using the SIT; but without reinterpreting them prior to this extrapolation (the result of this extrapolation was then not considered by the present review). They proposed (see the table) a $\beta_1°$ value that is not in accord with the value determined by this review, and $\Delta\varepsilon_1$ which is in fair agreement with the value proposed by this review.

Neck, Runde, Kim and Kanellakopulos also reported β_1 and β_2 values deduced from absorption spectrophotometry [94NEC/RUN]. The k_2 value (calculated as β_2/β_1) is exactly the same one as they reported from their solubility measurements in the same paper, and it is in accord with the value proposed by the present review; while their β_1 value is

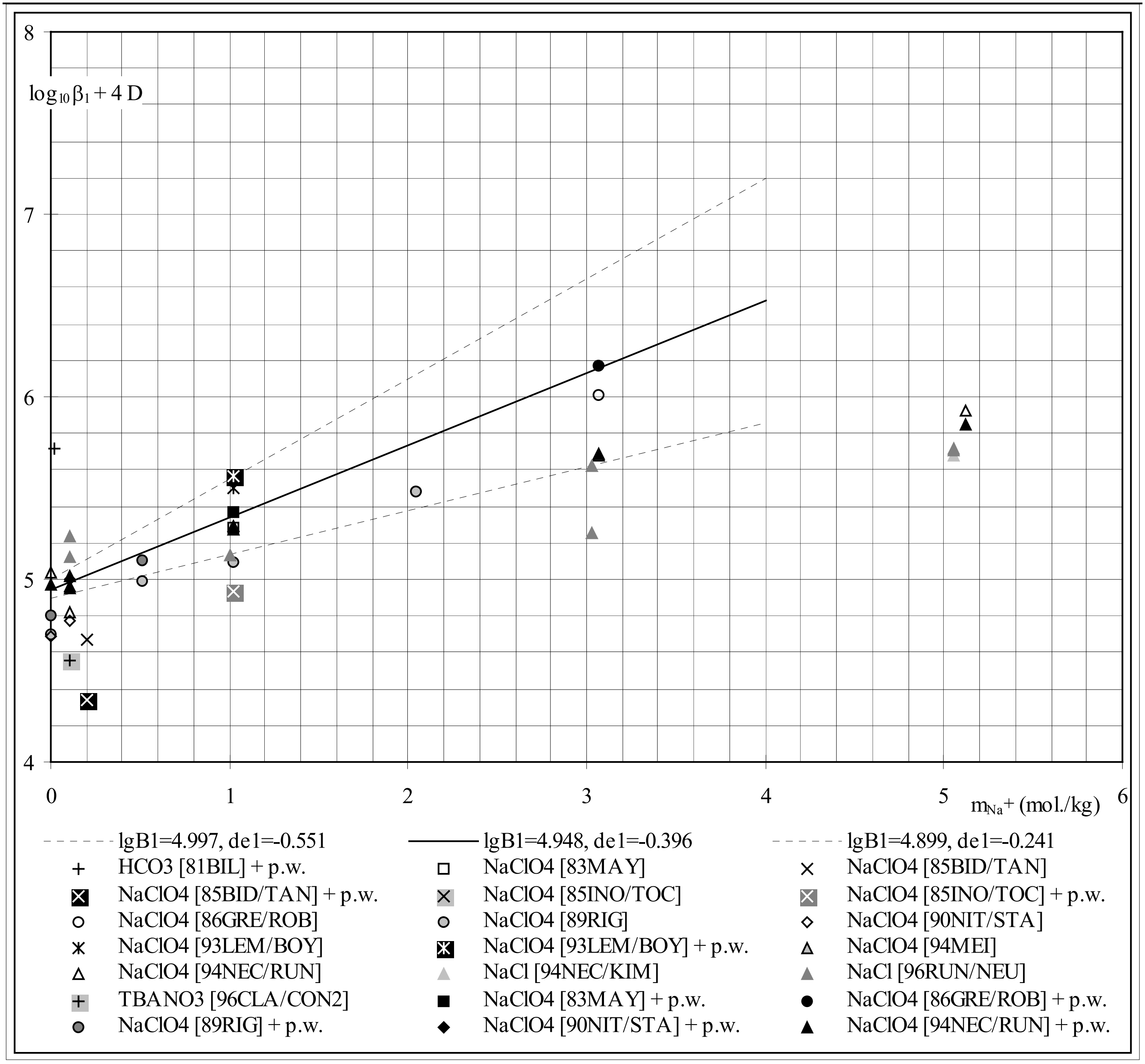


Figure A: Extrapolation to I =0 of the NpO_2^+ + CO_3^{-2} ⇔ $NpO_2CO_3^-$ equilibrium constant gave lgB1 = **$\log_{10}\beta_1°$ =4.94_8 ± 0.04_9** = and **$\Delta\varepsilon_1$ = -0.39_6 ± 0.15_5 kg.mol.$^{-1}$** = $\varepsilon(Na^+,NpO_2CO_3^-)$ - $\varepsilon(NpO_2^+,ClO_4^-)$ - $\varepsilon(Na^+,CO_3^{-2})$ = de1, using the SIT (see the appendix B) on the data of the [83MAY]+p.w., [86GRE/ROB]+p.w., [89RIG]+p.w, [90NIT/STA]+p.w. and [94NEC/RUN]+p.w. references in respectively 1, 3, 0.5, 0.1 and 0 M $NaClO_4$ aqueous solutions. +p.w. means reinterpreted by this review (see the appendix A). Other literature experimental data (that were not considered by this review for the reasons indicated in the text and the appendix A) are also plotted for comparison.

not consistent (within the uncertainty estimated by the authors) with the value they determined from their solubility measurements (see the discussion of the [91KIM/KLE] report in the appendix A) in contradiction with what they claimed in the [94NEC/RUN] publication. There was then a problem with this work; but there was not enough experimental information to reinterpret the spectrophotometric measurements, this review then did not consider the corresponding data.

Clark et al. [96RUN/NEU] also reported β_1 and β_2 values deduced from absorption spectrophotometry from about 30 to 70°C. At 25°C, the β_1 one is not in accord with the value selected by this review within the uncertainty estimated by the authors; while the k_2 one is. It was not considered by this review because there was not enough information in this publication.

Complexing constants were also determined in several solubility studies in $NaClO_4$ or NaCl aqueous solutions. There are problems with the solid phase, that are explained below when selecting solubility product. This should not have direct influence on the selection of the stepwise complexing constant. This problem is then not discussed here. Another problem is that the formation of the $NpO_2CO_3^-$ complex, corresponds to a constant minimum Np(V) solubility which is not far from usual detection limits (for α or γ spectrometry or liquid scintillation); but it does not seem that it was a problem in any of the examined publications.

This review found several small problems when checking Kim's or his co-author's solubility measurements (see the discussion of the [91KIM/KLE and 94NEC/RUN] publications in the appendix A) that possibly induced systematic deviation at high ionic strength, where the carbonic gas acidic constant measured in those works, was not in accord with published ones, neither with the thermodynamic auxiliary data used by this review. The methodology used by this

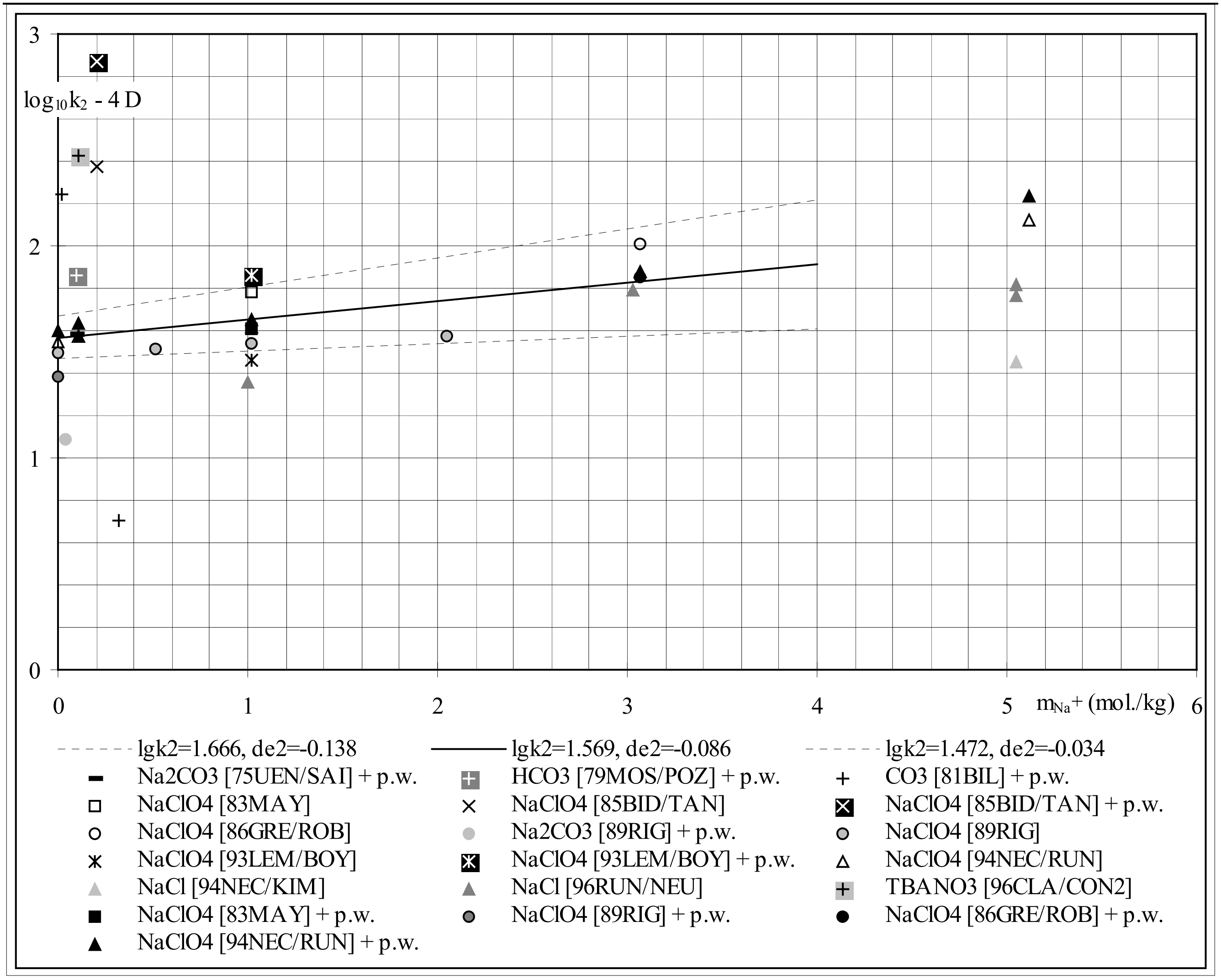


Figure B: Extrapolation to I =0 of the $NpO_2CO_3^-$ + CO_3^{-2} ⇔ $NpO_2(CO_3)_2^{-3}$ equilibrium constant gave $\log_{10}\beta_2°/\beta_1°$ = lgk2 = **$\log_{10}k_2°$ = $1.56_9 \pm 0.09_7$** and **$\Delta\varepsilon_2$ = $-0.08_6 \pm 0.05_2$ kg.mol.$^{-1}$** = $\varepsilon(Na^+,NpO_2(CO_3)_2^{-3}) - \varepsilon(Na^+,NpO_2CO_3^-) - \varepsilon(Na^+,CO_3^{-2})$, using the SIT (see the appendix B) on the data of the [83MAY]+p.w., [86GRE/ROB]+p.w., and [94NEC/RUN]+p.w. references in respectively 1, 3, and 0 M $NaClO_4$ aqueous solutions. +p.w. means reinterpreted by this review (see the appendix A). Other literature experimental data (that were not considered by this review for the reasons indicated in the text and the appendix A) are also plotted for comparison. TBA is tetrabutylammonium.

laboratory was not classical and possibly not completely understood by the present review. It seems that they might have used wrong definition of pH, and of activity coefficient. Their results were neither consistent with the NpO_2^+ activity coefficient used in the present review, neither with the one that some of the authors estimated in another publication (see the discussion of the [94NEC/RUN, 95NEC/FAN and 96RUN/NEU] publications in the appendix A) and that was in accord with the present review. So among the values produced by Kim or his co-authors, this review only used the one extrapolated to zero ionic strength, where the above systematic deviations seemed to cancel.

The Np(V) solubility tabulated in the [91KIM/KLE] report for I = 1 M ($NaClO_4$), can exactly be plotted on the same curve as the previous Maya's one [83MAY]; but the pH calibration was possibly not the same in both works. If the authors did not shift their curve for calibration, this means that the same solid phase was controlling the solubility in both works. This is clear for the minimum solubility that does not depend on pH calibration.

The complexing constant value selected at I = 3 M ($NaClO_4$) is important for extrapolation to zero ionic strength, because they have critical influence on the Δε values. The Np(V) solubility tabulated in the [91KIM/KLE] report or shown in other works by Kim's or his co-authors [94NEC/KIM, 94NEC/RUN, 95FAN/NEC, 95NEC/RUN and 96RUN/NEU] are a little shifted toward higher [CO_3^{-2}] when compared with Grenthe, Robouch and Vitorge's previous data [86BRE/ROB]. This shift cannot be explained by only differences in pH calibration, because in the same chemical condition, this shift was more important for hydrated $Na_3NpO_2(CO_3)_{2(s)}$ compound solubility, than for $NaNpO_2CO_{3(s)}$ one. This review estimated that it was an evidence that the solubility was not controlled by the same solid phases in both works (see the discussion on the selection of solubility product). There was then possibly two reasons to find differences between the two works: this chemical difference in the solid phase, and the above possible error in pH calibration by Kim or his co-authors. So this review had to rely only on the [86BRE/ROB] measurements at I = 3 M assuming that there was no other systematic deviation in this work. From their solubility measurements, Kim et al. [91KIM/KLE and 94NEC/KIM] extrapolated Np(V) carbonate complexing constants to zero ionic strength by using the SIT. This review checked these extrapolations (see the table). Their $\beta_1°$ determinations, and the corresponding $\Delta\varepsilon_1$ are in poor agreement with the value proposed by the present review. This is mostly due to the difference with the data selected at I = 3 M from the [86GRE/ROB] publication that is different by 0.45 $\log_{10}$ unit from Kim's et al determination (see above). Both data at I = 3 M are in accord because this

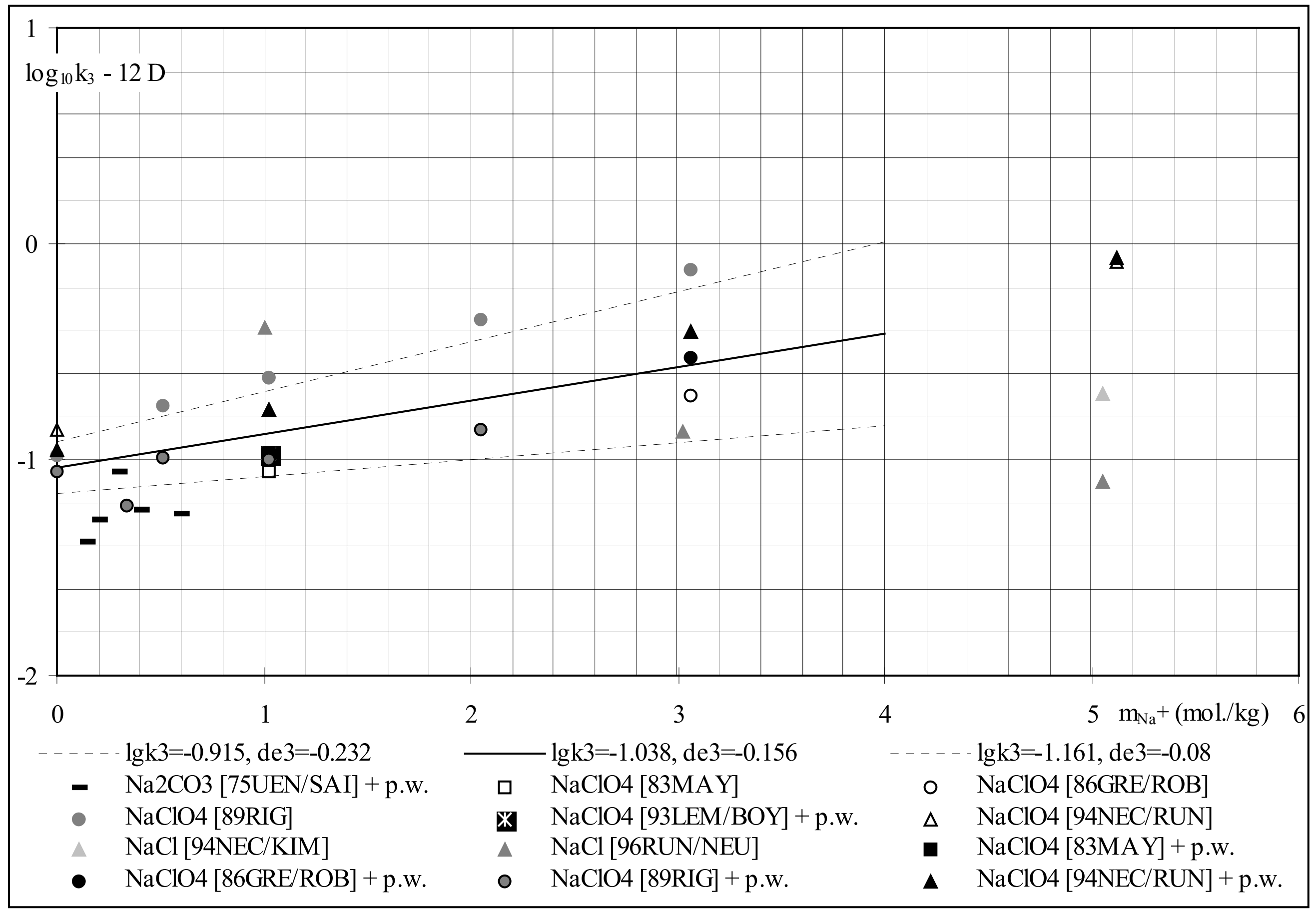


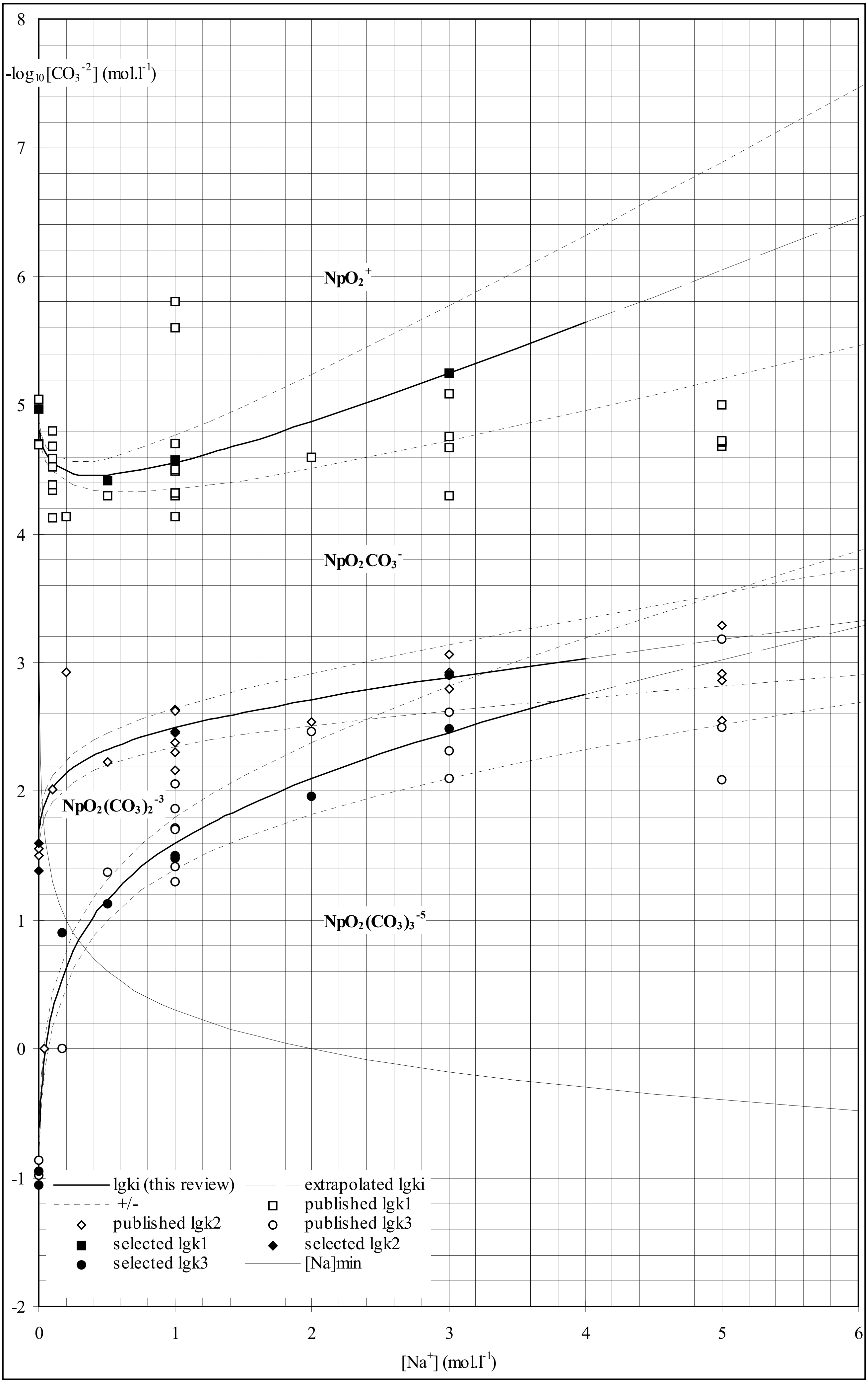
Figure C: Extrapolation to I =0 of the $NpO_2(CO_3)_2^{-3}$ + CO_3^{-2} ⇔ $NpO_2(CO_3)_3^{-5}$ equilibrium constant gave lgk3 = $\log_{10}\beta_3°/\beta_2°$ = **$\log_{10}k_3°$ = -1.03$_8$ ± 0.12$_3$** and **$\Delta\varepsilon_3$ = -0.15$_6$ ± 0.07$_6$ kg.mol.$^{-1}$** = $\varepsilon(Na^+,NpO_2(CO_3)_3^{-5})$ - $\varepsilon(Na^+,NpO_2(CO_3)_2^{-3})$ - $\varepsilon(Na^+,CO_3^{-2})$ = de3, using the SIT (see the appendix B) on the solubility data of the [83MAY]+p.w., [86GRE/ROB]+p.w., and [94NEC/RUN]+p.w. references in respectively 1, 3, and 0 M $NaClO_4$ aqueous solutions, and of the [89RIG]+p.w one in 0.5, 1 and 2 M $NaClO_4$ aqueous solutions. +p.w. means reinterpreted by this review (see the appendix A). Other literature experimental data (that were not considered by this review for the reasons indicated in the text and the appendix A). TBA is tetrabutylammonium.

review increased the uncertainty of Kim's work, to 0.42 for possible systematic error in pH calibration.

On the author hand, there is not this problem for the values of k_2 and k_3 stepwise complexing constants extrapolated to zero ionic strength and the corresponding $\Delta\varepsilon_2$ and $\Delta\varepsilon_3$ as extrapolated to I = 0 by this review. Two different $k_3°$ values were given by Kim et al. in his two publications [91KIM/KLE and 94NEC/KIM], he did not explain this inconsistency. The above pH calibration problems cannot then stand: it was possibly not much more than the uncertainty, or cancelled. The above (relatively small) inconsistency in the β_1 values should rather be attributed to problems in the solid compounds when equilibrated in aqueous solutions corresponding to the minimum solubility where these problems were found to be the most important. This review extrapolated to zero ionic strength each stepwise equilibrium constant from Kim et al. data (see the table) and only used this data from Kim's et al. works for the reason explained above: systematic error was suspected at high ionic strength in the data by Kim or his co-authors. This means that his ionic strength corrections were not considered at all. It should be noted that they are still in accord with the data proposed by this review for the ionic strength corrections on the k_2 and k_3 constants.

The first set of equilibrium constants for Np(V) carbonate complexes was proposed by Maya [83MAY] from its solubility measurements in 1 M $NaClO_4$ aqueous solution, and confirmed by Grenthe, Robouch and Vitorge [86GRE/ROB] that used the same technique in 3 M $NaClO_4$ aqueous solutions. Using the SIT, extrapolation to zero ionic strength from these two determinations gave stepwise complexing constants, $k_i°$, and the corresponding $\Delta\varepsilon_i$ values in accord with those selected by this review (see the table).

Figure D (next page): **Predominance diagrams of Np(V) carbonate aqueous complexes** at different ionic strengths in $NaClO_4$ aqueous solutions. The lines are calculated with the data selected by this review: they are the stepwise formation constants that were then also directly measured (points on the figure). Ionic strength correction can be less than the scattering of the data. $NpO_2(CO_3)_2^{-3}$ is not stable at high ionic strength, while $NpO_2(CO_3)_3^{-5}$ can be formed only at high ionic strength. The domain below the [Na]min line cannot be obtained experimentally: the k_3 values drawn in this domain were extrapolated or measured in chemical conditions where less than 50 % of the limiting complex ($NpO_2(CO_3)_3^{-5}$) was formed. Dashed lines account for error propagation when recalculating $\log_{10}k_i$ from $\log_{10}k_i°$ and $\Delta\varepsilon_i$ (while direct measurements were usually more accurate).


-log$_{10}$[CO_3^{-2}] (mol.l^{-1})
8
7
6
5
4
3
2
1
0
-1
-2
0
1
2
3
4
5
6
[Na^+] (mol.l^{-1})
NpO_2^+
$NpO_2CO_3^-$
$NpO_2(CO_3)_2^{-3}$
$NpO_2(CO_3)_3^{-5}$
lgki (this review)
extrapolated lgki
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published lgk1
published lgk2
published lgk3
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selected lgk3
[Na]min

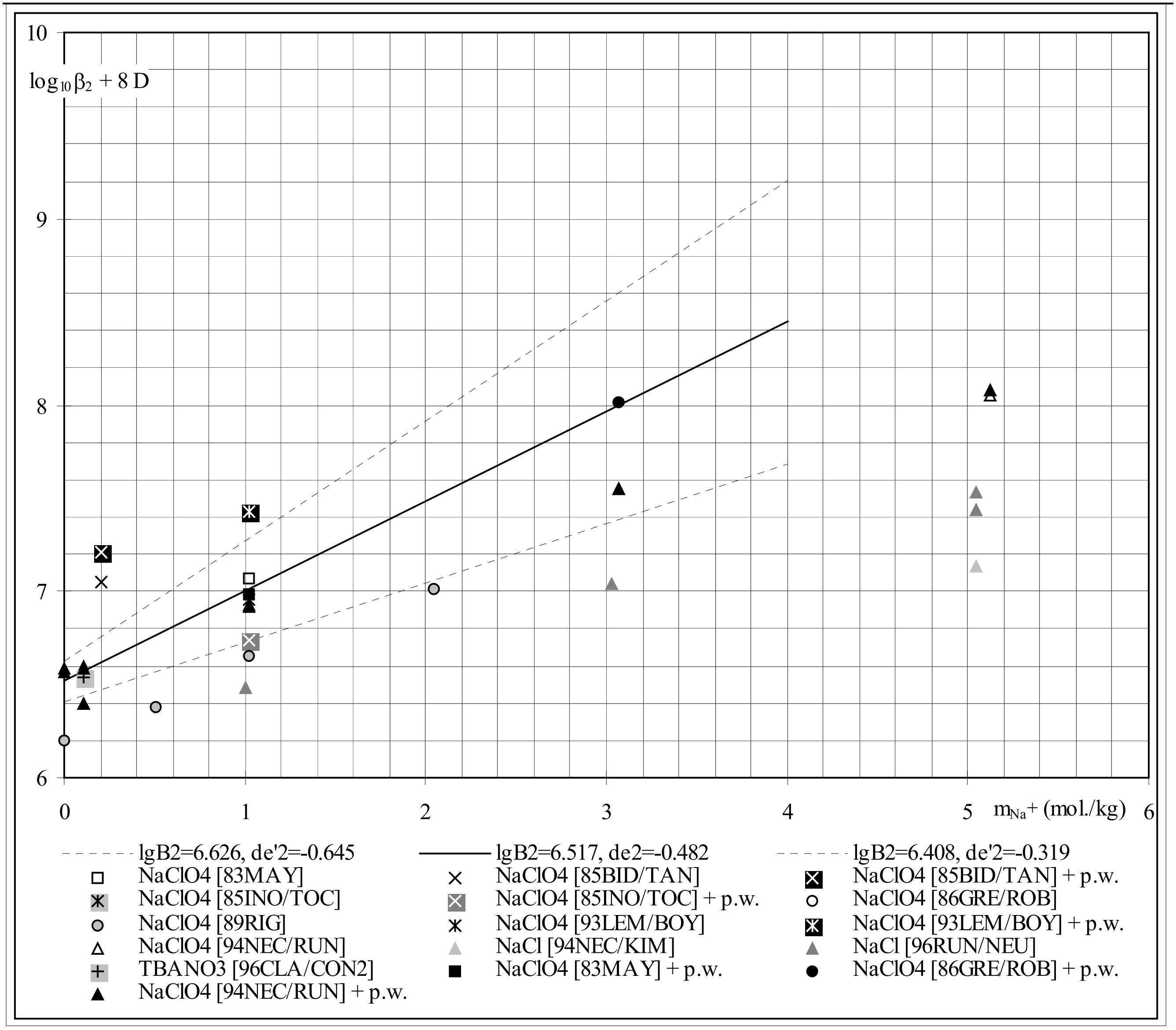


Figure E: Comparison of values of the $NpO_2^{+} + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$ classical equilibrium constant, $\beta_2 = k_1\ k_2$. These literature experimental data are plotted for comparison. The lines are calculated with the data selected in the present review for k_1 and k_2 (figures A and B). de'2 = $\varepsilon(Na^+,NpO_2(CO_3)_2^{-3})$ - $\varepsilon(NpO_2^+,ClO_4^-)$ - 2 $\varepsilon(Na^+,CO_3^{-2})$ = **$\Delta\varepsilon'_2 = -0.48_2 \pm 0.16_3$ kg.mol.$^{-1}$** and **$\log_{10}\beta_2° = 6.51_7 \pm 0.19_4$** = gB2. TBA is tetrabutylammonium.

For β_1 this selection was obtained in the same way (SIT non weighted linear regression); but adding to these [83MAY and 86GRE/ROB] solubility data, those of Kim et al. [91KIM/KLE, 94NEC/KIM, 94NEC/RUN] reextrapolated to I = 0 (see the appendix A) and the spectrophotometric determinations of Riglet [89RIG], and of Nitsche, Standifer and Silva [90NIT/TAN] in 0.5 and 0.1 M $NaClO_4$ aqueous solutions respectively, both reinterpreted by this review as explained above (see also the appendix A). As explained above, the liquid-liquid extraction data were not considered. The selected value is obtained from unweighted linear regression:

$\log_{10}\beta_1°$ = 4.95 ± 0.18

1.96 σ = 0.05 was calculated (eliminating Kim's at al. data, because calibration error was suspected at high ionic strength as explained above), but uncertainty has been increased to 0.18 accounting for the discrepancy of Kim's et al. data with [86GE/ROB] ones (explained above) though these works were in concentrated (3 M) $NaClO_4$ aqueous solutions, and though this uncertainty was already reflected in the corresponding detalEpsilon1 value.

Linear regression also gives $\Delta\varepsilon_1$ = (-0.40 ± 0.16) kg.mol.-1 (Figure A). Using this last value, $\varepsilon(Na^+,CO_3^{-2})$ = (-0.08 ± 0.3) kg.mol.$^{-1}$ and $\varepsilon(NpO_2^+,ClO_4^-)$ = (0.25 ± 0.05) kg.mol.-1 the new interaction coefficient is deduced: $\varepsilon(Na^+,NpO_2CO_3^-)$ = (-0.23 ± 0.17) kg.mol.$^{-1}$. $\log_{10}\beta_1°$ = 4.95 ± 0.18 corresponds to

$\Delta_rG_{1m}°$ = (-28.24 ± 1.03) kJ.mol.$^{-1}$

For k_2 this selection was obtained from [83MAY and 86GRE/ROB] solubility data, those of Kim et al. [91KIM/KLE, 94NEC/KIM, 94NEC/RUN] reextrapolated to I = 0 by this review, excluding the data at I = 5 M where the SIT is usually no more valid. Ionic strength corrections deduced from only Riglet's spectrophotometric data are in accord with this selection. It should be noted that Kim et al. data up to I = 5 M are still in accord with those selected by this review. The spectrophotometric determinations of Riglet [89RIG], in 0.5, 1 and 2 M $NaClO_4$ aqueous solutions respectively where not used (see above); but it should be noted that they are in accord with the results proposed by this review. The liquid-liquid extraction data were not considered; but it should be noted that those proposed by Inoue and Tochiyama [85INO/TOC] at I = 1 M are in reasonable agreement with the results proposed by this review. The selected values were obtained from unweighted linear regression:

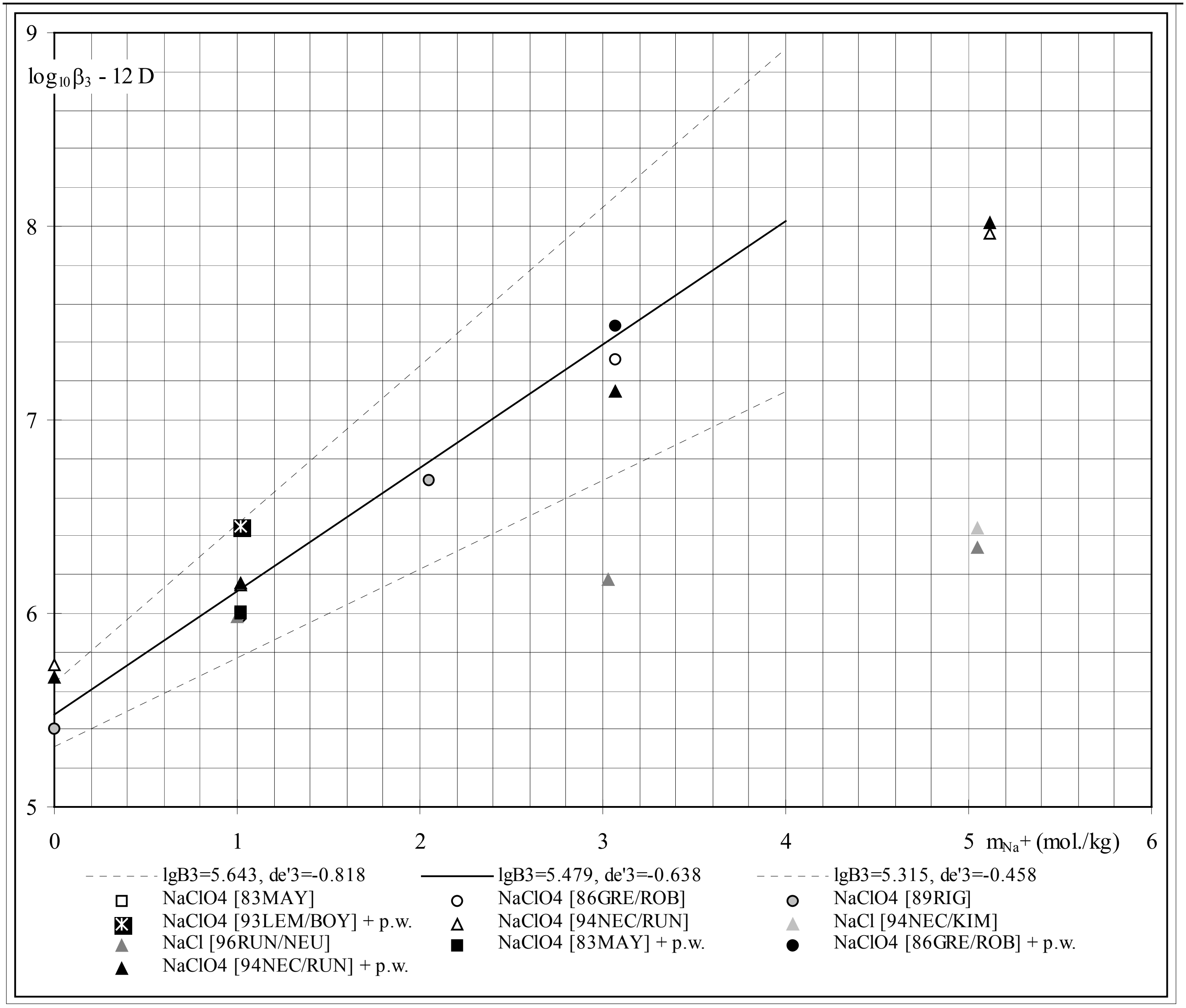


Figure F: Comparison of values of the $NpO_2^+ + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$ classical equilibrium constant, $\beta_3 = k_1\ k_2\ k_3$. These literature experimental data are plotted for comparison. The lines are calculated with the data selected in the present review for k_1, k_2 and k_3 (figures A, B and C). de'3 = $\varepsilon(Na^+,NpO_2(CO_3)_3^{-5}) - \varepsilon(NpO_2^+,ClO_4^-) - 3\ \varepsilon(Na^+,CO_3^{-2})$ = **$\Delta\varepsilon'_3 = -0.63_8 \pm 0.18_0$ kg.mol.$^{-1}$, $\log_{10}\beta_3^\circ = 5.47_9 \pm 0.16_4$** = lgB3. TBA is tetrabutylammonium.

$$\log_{10}K_2^\circ = 1.57 \pm 0.10$$

Linear regression also gives also gives the corresponding $\Delta\varepsilon_2$ = (-0.09 ± 0.05) kg.mol.$^{-1}$ (Figure B). Using this last value, as above the new interaction coefficient is deduced: $\varepsilon(Na^+,NpO_2(CO_3)_2^{-3})$ = (-0.39 ±0.18) kg.mol.-1. $\log_{10}K_2^\circ = 1.57 \pm 0.10$ corresponds to

$$\Delta_rG_{2m}^\circ = (-8.96 \pm 0.55)\ kJ.mol.^{-1}$$

From the above β_1 and k_2 values selected by this review, one deduces $\beta_2 = \beta_1\ k_2$:

$$\log_{10}\beta_2^\circ = 6.52 \pm 0.20$$

and the corresponding

$$\Delta_rG_{2m}^{\circ\prime} = (-37.20 \pm 1.17)\ kJ.mol.^{-1}$$

For k_3 this selection was obtained from [83MAY and 86GRE/ROB] solubility data, those of Kim et al. [91KIM/KLE, 94NEC/KIM, 94NEC/RUN] reextrapolated to I = 0 by this review, and the spectrophotometric determinations of Riglet [89RIG] in 0.5 to 2 M $NaClO_4$ aqueous solutions as reinterpreted by this review. Ionic strength corrections deduced from only Riglet's spectrophotometric data are in accord with this selection. More weight was then given to a single laboratory [86GRE/ROB and 89RIG]; this was done to equilibrate the selection between spectrophotometric and solubility techniques. In this particular case, solubility measurements were obtained for metastable equilibrium, Maya's data include practically only one measurement needed of the k_3 determination. The selected value was obtained from unweighted linear regression:

$$\log_{10}K_3^\circ = -1.04 \pm 0.12$$

Linear regression also gives the corresponding $\Delta\varepsilon_3$ = (-0.16 ± 0.08) kg.mol.-1 (Figure C). Using this last value, as above the new interaction coefficient is deduced: $\varepsilon(Na^+,NpO_2(CO_3)_3^{-5})$ = (-0.63 ± 0.21) kg.mol.-1. $\log_{10}K_3^\circ = -1.04 \pm 0.12$ corresponds to

$$\Delta_rG_{3m}^\circ = (+5.92 \pm 0.70)\ kJ.mol.^{-1}$$

From the above β_1, k_2 and k_3 values selected by this review, one deduces $\beta_3 = \beta_1\ k_2\ k_3$:

$$\log_{10}\beta_3^\circ = 5.48 \pm 0.24$$

and the corresponding

$$\Delta_rG_{3m}^{\circ\prime} = (-31.27 \pm 1.37)\ kJ.mol.^{-1}$$

The above complexing constants indicate, that CO_3^{2-} ligand affinity for Np(V) is nearly as important as for Am(III) : this is quite an exception since Np(V) reactivity toward oxygen donors is usually much smaller, that is typically the case for OH^-. Carbonate complexation is then of relatively high importance for practical applications.

b) Temperature influence on Np(V) carbonate complexes

Gorbenko-Germanov and Zenkova reported [66GOR/ZEN] Np(V) solubility at 20 and 80°C; but it cannot be known whether the solid phase was the same in the two measurements. This review did not then use these measurements to propose thermodynamic data, neither any temperature influence on solubility for the reasons explained below when selecting solubility products.

Lemire, Boyer and Campbell studied Np(V) solubility in alkali-carbonate media at 30 to 75°C [93LEM/BOY]. Practically constant solubility in a wide domain of chemical conditions was found. This was due to the opposite effects of carbonate complexation (that increased solubility with $[CO_3^{-2}]$), and solid phase transformations that were difficult to control. Curve fitting performed by the author was difficult on such flat curves. This review rather tried graphical interpretation (see the appendix A), and for the same reason as at 25°C (see above), only considered stepwise formations constants of the soluble complexes. This was a rough interpretation, and this review attributed a poor accuracy to its interpretation. Both treatments could give different trends, certainly because temperature variations were less than the actual accuracy. Lemire, Boyer and Campbell β_1, k_2 and k_3 determinations at 30°C are still in reasonable agreement was those selected by this review at 25°C.

Clark et al. [96CLA/CON2] used a spectrophotometric technique to propose β_1 and β_2 temperature variations. They refer to another ("submitted" to Inorganic Chemistry) publication that was not available to the present review, and to the background provided in the [94NEC/RUN] publication which was not considered by the present review, while more accurate spectrophotometric data were available (see the above discussion of the selection of the aqueous Np(V) carbonate complexes at 25°C). They showed a figure with accurate complexing constants, and linear variations of their log formation constant with 1/T, and deduced ΔH values. There is no way to check these measurements and treatment of the data at each temperature. The β_1 and k_2 determinations at 25°C are not in accord with those selected by the present review while β_2 is. This review did not then consider these data; but it should be noted that the method used in this work is promising, even at 25°C where there are still problems with the selection of the $NpO_2CO_3^-$ formation constant molar aborptivity and specially activity coefficient.

This review calculated the following values from its revaluation of Lemire and Boyer's work (see the discussion of the [93LEM/BOY] publication in the appendix A); the corresponding data of the [96CLA/CON2] publication are shown for comparison.

ΔH_1 = 19 ±138 kJ.mol^{-1} (-15.9 ±0.5 [96CLA/CON2])
ΔH_2 = -27 ± 91 kJ.mol^{-1} (0.3 ±0.5 [96CLA/CON2])
ΔH_3 = 4 ± 42 kJ.mol^{-1}

c) Mixed Np(V) hydroxide-carbonate complexes

Varlashkin, Begun and Hobart [84VAR/BEG and 84VAR/HOB] observed Np(V) spectral variations when adding concentrated NaOH to concentrated Na_2CO_3 aqueous solutions. Riglet reproduced this observation and studied this system [89RIG]. She showed that it was an evidence of the formation of mixed hydroxide-carbonate-complex. She suggested the formation of the $NpO_2OH(CO_3)_2^{-4}$ and $NpO_2(OH)_2CO_3^{-3}$; but said that the stoichiometry could not be proven. Other possible interpretation is rather the dissociation of the limiting carbonate complex, $NpO_2(CO_3)_3^{-5}$, according to

$$NpO_2(CO_3)_3^{-5} + 2\ OH^- \Leftrightarrow NpO_2(OH)_2(CO_3)_2^{-5} + CO_3^{-2}$$

$NpO_2(OH)_2(CO_3)_2^{-5}$ concentration still decreased with increasing pH, which could be due to precipitation, $NpO_2(OH)_2^-$ formation, or the formation of another soluble complex, possibly $NpO_2(OH)_2CO_3^{-3}$. From half point reaction the constant of the above equilibrium is

$\log_{10}K$ = 0.8_4 ± 1.3

Np(III) carbonate complexes

Np^{3+} can be prepared and stabilised in non complexing (acidic) reducing aqueous solution. For kinetic reasons Np(III) is certainly in most of the cases, an intermediary species, when preparing Np(IV) in carbonate solutions (see the discussion of the [84VAR/HOB] publication in the appendix A and the [95VIT and 95DEL/VIT] papers). Nevertheless, Np(III) complexes that might be formed in carbonate aqueous solutions, are possibly not much thermodynamically stable. As for Am^{3+} [95SIL/BID], Np^{3+} cation is expected to be complexed by the carbonate anion in near neutral or basic aqueous solutions. In these conditions $Np(OH)_{4(aq)}$ or other Np(IV) complexes strongly stabilise neptunium at the +4 oxidation state, and Np(III) is usually oxidised to Np(IV) by water. For this reason, there are not any reliable experimental study, that could be used to propose thermodynamic data on the formation of Np(III) complexes in bicarbonate / carbonate media. This review then did not select any. As a guide line, complexing constants of americium [95SIL/BID] or lanthanide chemical analogues could be used as reasonable approximations.

VI.7.1.2 Solid alkali-neptunium(V) hydrated carbonates

Preparation of a hydrated $KNpO_2CO_{3(s)}$ solid by Nigon, Penneman, Staritzky et al. [54NIG/PEN] is the first publication on neptunium chemistry in carbonate media. Keenan and Kruse later characterised a compound with the same stoichiometry [64KEE/KRU]. Keenan [65KEE] claimed that he prepared a $CsAmO_2CO_{3(s)}$ compound; but not the corresponding Np(V)

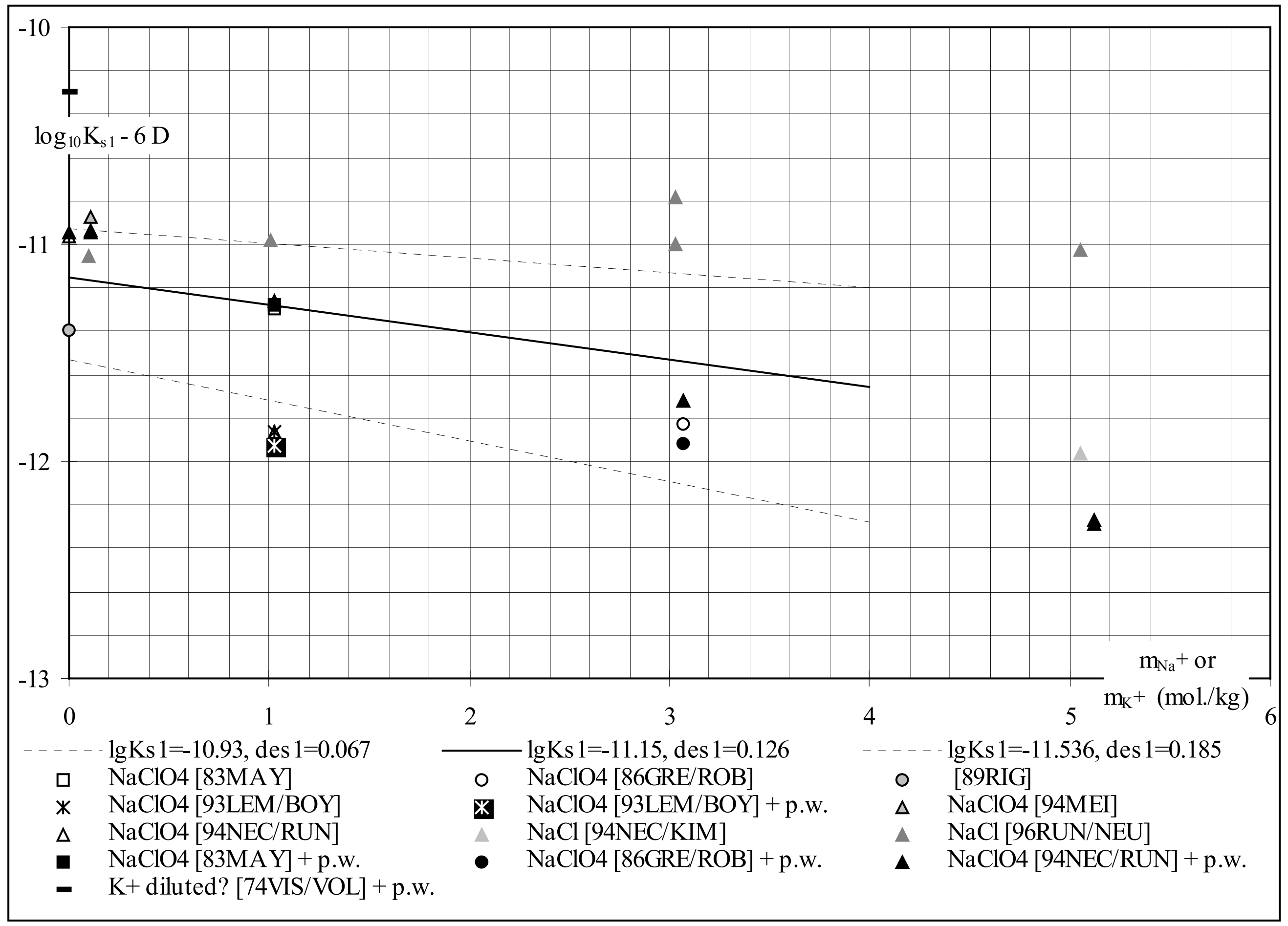


Figure G: **Comparison of $NaNpO_2CO_{3(s)}.xH_2O \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{-2} + x\ H_2O$ solubility product**, K_{s1}, directly measured at different ionic strengths in chemical conditions where NpO_2^+ contribution to the solubility is high enough about -4 > ($log_{10}[CO_3^{-2}]$). D is the Debye-Hückel term (see the appendix B). The scattering of the published data is mainly due to solid phase transformation, for this reason, SIT regression was not used (see the text). The lines are calculated (only for Na^+ media) with the data selected by this review (see the appendix B) for des1 = $\mathbf{\Delta\varepsilon_{s1} = 0.12_6 \pm 0.05_9}$ **kg.mol.$^{-1}$** = $\varepsilon(Na^+,ClO_4^-) + \varepsilon(NpO_2^+,ClO_4^-) + \varepsilon(Na^+,CO_3^{-2}) + 3.5\ r$ (where r is $log_{10}a_{H2O}$ / m mean value), and from the [83MAY and 86GRE/ROB] determinations in 1 and 3 M $NaClO_4$ aqueous solutions (extrapolated to I=0 by using $\Delta\varepsilon_{s1} = 0.12_6$ kg.mol.$^{-1}$) and only from the data at I = 0 from the [94NEC/RUN] work $\mathbf{log_{10}K_{s1}° = -11.15 \pm 0.59}$ = lgKs1. The other values are shown for comparison. The solid line corresponds to freshly precipitated hydrated compound, where x = 3.5 is the most probable value, while the dashed lines give an idea of uncertainty including aged compound, possibly dehydrated. [93LEM/BOY] determination was at 30°C while the other ones are at room temperature. +pw means as re-evaluated by this review.

that should be easier to prepare (see the appendix A). Gorbenko-Germanov and Zenkova [66GOR/ZEN] precipitated M-Np(V)-CO3 solid compounds, for M = K or Cs, with different stoichiometries including $K_3NpO_2(CO_3)_{2(s)}$; but this review estimated that the equilibrium was probably not obtained, and the hydrated solid phases were changing in the course of the experiments (see the appendix A). Moskvin prepared a $NH_4NpO_2CO_{3(s)}$ hydrated compound [71MOS5], and he studied with Kharitonov its infrared spectrum [73KHA/MOS]; but the compound was not characterised, and Moskvin did not understand (and then properly controlled) its behaviour in contact with concentrated aqueous solutions of $(NH_4)_2CO_3$ (i.e. bicarbonate / carbonate buffers). This solid was certainly transformed into another (more stable) one (as reinterpreted by this review: see the Appendix A), possibly a hydrated $(NH_4)_3NpO_2(CO_3)_{2(s)}$ compound, when $(NH_4)_2CO_3$ concentration was more than 1.5 M, and possibly more than 0.6 M (see the appendix A). Volkov et al. later proposed the structure of this type of alkaline carbonate compounds for Np(V), Pu(V) and Am(V), where the alkaline cation could be exchanged for the NH_4^+ or possibly divalent ones; but in this series of publication (starting by the [74VIS/VOL] one and finishing with the [81VOL/VIS4] one) some propositions need confirmations (see the appendix A).

Simakin is the first author who used this qualitative information to measure and interpret with a correct methodology a solid / liquid equilibrium in Np(V) carbonate system. He studied the

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ Na^+$$

equilibrium. This review calculated the corresponding $K_{s2,3}$ equilibrium constant (see the appendix A) and used this value.

First (but indirect) evidence that solubility measurements could be used to estimate the $NaNpO_2CO_{3(s)}$ solubility product (and then ΔG_r) came from Ueno and Saito [75UEN/SAI] as interpreted by this review in the appendix A (the authors did not interpret their observations). Their solubility measurements in 0.05 to 0.4 M Na_2CO_3 aqueous solutions could be reproduced with the thermodynamic data selected by this review from later works for aqueous Np(V) complexes (see above) for the

$$NaNpO_2CO_{3(s)} + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

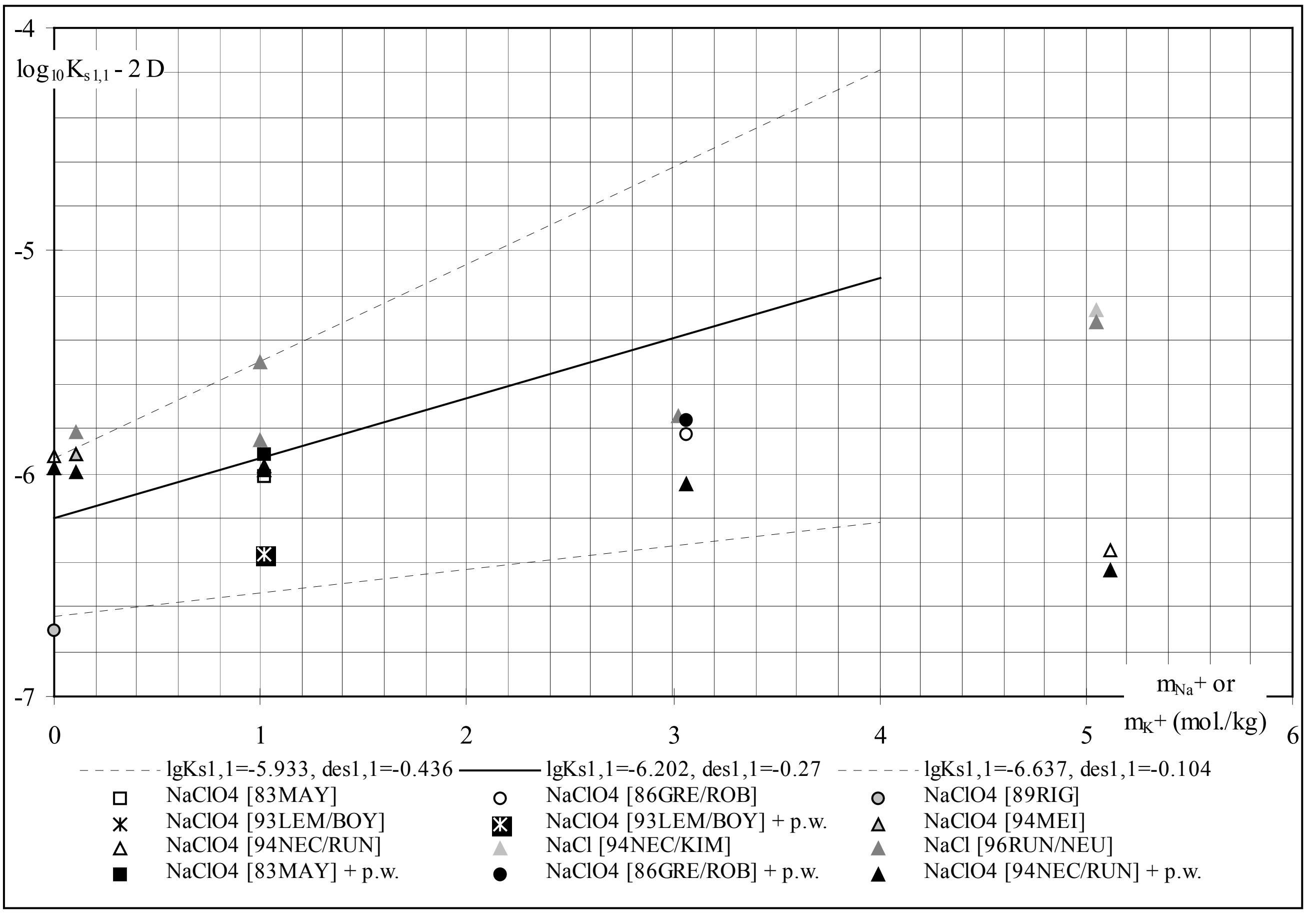


Figure H: Comparison of $NaNpO_2CO_{3(s)}.xH_2O \Leftrightarrow Na^+ + NpO_2CO_3^- + x\ H_2O$ equilibrium constant, $K_{s1,1}$, directly measured at different ionic strengths in chemical conditions where $NpO_2CO_3^-$ contribution to the solubility is high enough (about $-2 < \log_{10}[CO_3^{-2}] <$ about -5). D is the Debye-Hückel term (see the appendix B). lgKs1,1 = $\log_{10}(K_{s1}°\ \beta_1°)$ = **$\log_{10}K_{s1,1}° = -6.20_2 \pm 0.59_2$**, and **$\Delta\varepsilon_{s1,1} = -0.27_0 \pm 0.16_6$ kg.mol.$^{-1}$** = des1,1 = $\varepsilon(Na^+,ClO_4^-) + \varepsilon(Na^+,NpO_2CO_3^-) + 3.5\ r$ (where r is $\log_{10}a_{H2O}$ / m mean value). The scattering of the published data is mainly due to solid phase transformation, for this reason, SIT regression was not used (see the text). The lines are calculated with the data selected by this review for $\beta_1°$ and $\varepsilon(Na^+,NpO_2CO_3^-)$ (figure A), for $K_{s1}°$ (figure G) and auxiliary ε data (Appendix B). The solid line corresponds to freshly precipitated hydrated compound, where x = 3.5 is the most probable value, while the dashed lines give an idea of uncertainty including aged compound, possibly dehydrated. [93LEM/BOY] determination was at 30°C while the other ones are at room temperature. +pw means as re-evaluated by this review.

equilibrium, and the needed ionic strength correction. At higher Na_2CO_3 concentration corresponding to the above conditions, where Simakin prepared his $Na_3NpO_2(CO_3)_{2(s)}$ hydrated compound, equilibrium was not obtained prior to solubility measurements. $NpO_2(CO_3)_3^{5-}$ formation constant can be used to deduce the solubility product for the

$$NaNpO_2CO_{3(s)} \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{-2}$$

equilibrium; but better direct determinations were published.

$NaNpO_2CO_{3(s)}$

Maya [83MAY] first proposed a reliable solubility product value for a hydrated $NaNpO_2CO_{3(s)}$ compound in 1 M $NaClO_4$ aqueous solution. This review calculated practically the same solubility product as Maya's from his experimental solubility data; but increased uncertainty (see the appendix A). Only minor points were discussed (in the appendix A); and this review used Maya's solubility product.

Vitorge checked the $NaNpO_2CO_{3(s)}$ stoichiometry [84VIT] (see also the discussion of his other papers [85COM, 85KIM, 86GRE/ROB and 89RIG] in the appendix A). He pointed out that solid phase characterisation was not straightforward: the X-ray diffraction patterns of his compound should be attributed to the $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$ compound that received a thermal treatment as prepared by Volkov et al. [79VOL/VIS]. Since (as discussed just above) Volkov et al. proposed ionic exchange within the solid phase, Vitorge tested possible corresponding equilibrium with the aqueous phase according to

$$2\ (x-1)\ Na^+ + NaNpO_2CO_{3(s)} \Leftrightarrow Na_{2x-1}NpO_2(CO_3)_{x(s)} + (1-x)\ CO_3^{-2}$$

Solubility could be interpreted with a freshly precipitated hydrated $Na_{0.72}NpO_2(CO_3)_{0.86(s)}$ compound (where "freshly" means up to several weeks of equilibration: which is more than the time used in other published similar studies), but the $NaNpO_2CO_{3(s)}$ stoichiometry was obtained with time, or at least an x value that was not different from 1 within the 0.07 uncertainty (see the appendix A).

This confirms that at least some of the solid compounds prepared by Volkov's group were poorly crystallised, and that equilibrium conditions with an aqueous phase were not always obtained. For $MNpO_2CO_{3(s)}$ compounds, x-ray diffraction patterns were usually interpreted (with a proposed structure); but single crystal has never been prepared. Since these x-ray diffraction patterns have many rays, this could reflect low symmetry, as well as bad crystallisation or even

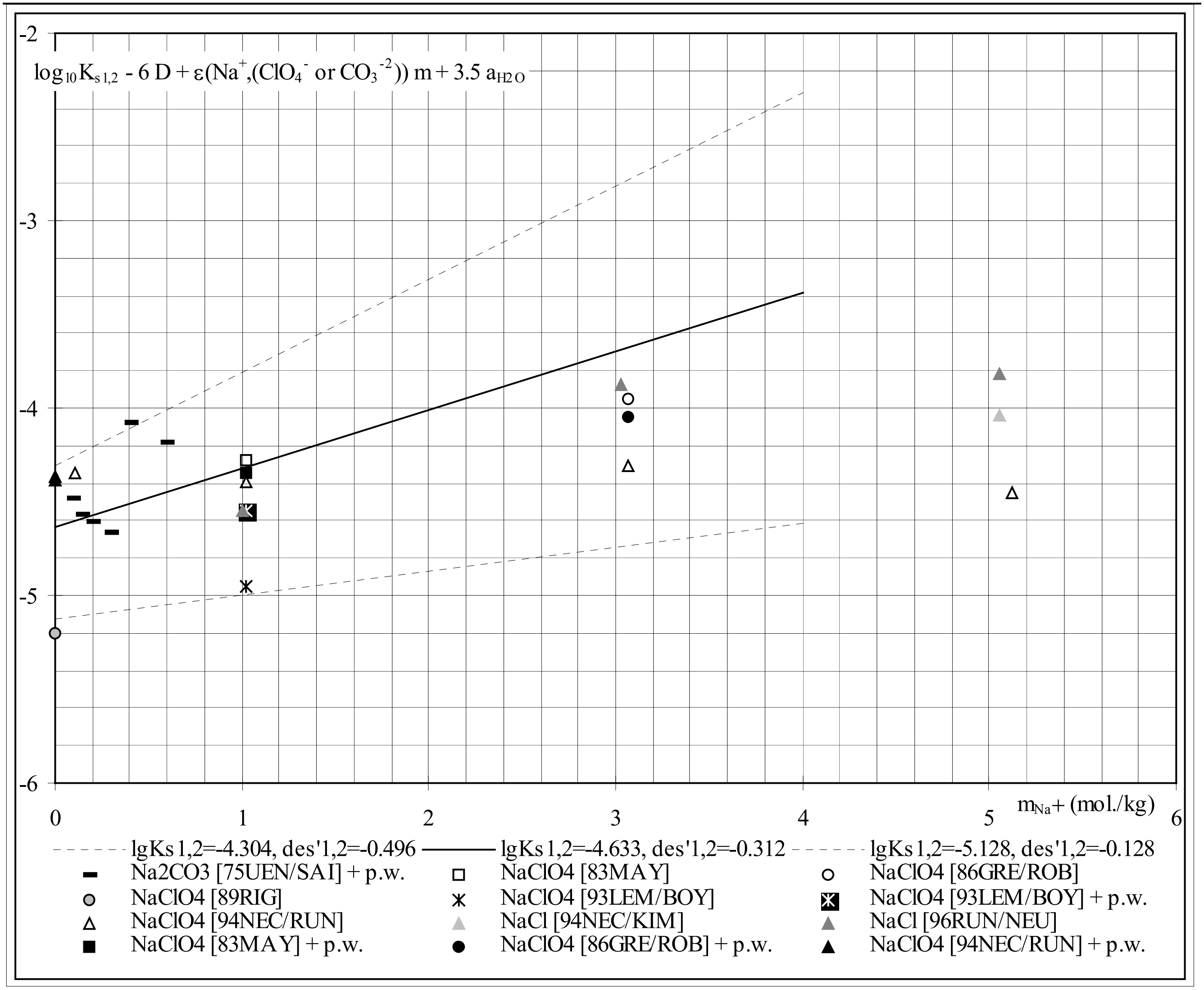


Figure I: **Comparison of $NaNpO_2CO_{3(s)}.xH_2O + CO_3^{-2} \Leftrightarrow Na^+ + NpO_2(CO_3)_2^{3-} + x\ H_2O$ equilibrium constant**, $K_{s1,2}$, directly measured at different ionic strengths in chemical conditions where $NpO_2(CO_3)_2^{-3}$ contribution to the solubility is high enough ($\log_{10}[CO_3^{-2}] \approx -2$). $\log_{10}K_{s1,2}$ is corrected for Debye-Hückel term, D (see the appendix B), for water activity (a_{H2O}) and for $\varepsilon(Na^+,(ClO_4^-$ or $CO_3^{-2}))$, in this way the theoretical line calculated with the SIT formula is the same for $NaClO_4$ and Na_2CO_3 aqueous solutions. $lgKs1,2 = \log_{10}(K_{s1}°\ \beta_2°) = \log_{10}(K_{s1}°\ k_1°\ k_2°) =$ $\mathbf{\log_{10}K_{s1,2}° = -4.63_3 \pm 0.60_0}$, and $\mathbf{\Delta\varepsilon'_{s1,2} = -0.31_2 \pm 0.18_4}$ **kg.mol.$^{-1}$** = des'1,2 = $\varepsilon(Na^+,NpO_2(CO_3)_2^{3-}) - \varepsilon(Na^+,CO_3^{-2})$. The scattering of the published data is mainly due to solid phase transformation, for this reason, SIT regression was not used (see the text). The lines are calculated with the data selected by this review for $k_1°$ (figure A), for $k_2°$ and $\varepsilon(Na^+,NpO_2(CO_3)_2^{3-})$ (figure B), $K_{s1}°$ (figure G), and with ε auxiliary data (Appendix B). The solid line corresponds to freshly precipitated hydrated compound, where x = 3.5 is the most probable value, while the dashed lines give an idea of uncertainty including aged compound, possibly dehydrated. [93LEM/BOY] determination was at 30°C while the other ones are at room temperature. +pw means as re-evaluated by this review.

mixture of several compounds. Volkov et al. interpreted the variations between different x-ray diffraction patterns, with variation in the lattice distances, that could be correlated with the variations of the number of water molecules inside the compounds, some of them hydrating the alkaline cations (heavy alkaline cations are known to be usually less hydrated, than the light ones). This is a reasonable explanation; but this review estimated that more experimental confirmation is still needed. The proposed structure could also explain the ionic exchange property, but as discussed above, when the solid phase is in contact with aqueous solution, ionic exchange should rather be considered as a possible kinetic explanation of some experimental observations. These kinetic problems can induce variation in the solubility product measurements: lower values are expected for better crystalised (usually older then) solid phase. This is a classical problem. Fortunately these variations were finally not so important: about 1 $\log_{10}$ unit; but they can be more than ionic strength corrections.

Kim first had to summarise the above Vitorge's et al. observations within European collaboration [85COM and 85KIM] and later himself and co-workers made their own measurements [91KIM/KLE, 94MEI, 94NECK/KIM, 94NEC/RUN, 95FAN/NEC, 95NEC/FAN and 95NEC/RUN], that were not in accord with previous works (see the appendix A). As explained when selecting Np(V) aqueous carbonate species, this review suspected systematic deviation in the calibration procedures used in Kim's et al. works. Their was the same type of problem for their $NaNpO_2CO_{3(s)}$ solubility product, K_{s1}, determinations: the value of the corresponding $\Delta\varepsilon_1 = \varepsilon(Na^+,ClO_4^-) + \varepsilon(NpO_2^+,ClO_4^-) + \varepsilon(Na^+,CO_3^{-2})$ is known with reasonable accuracy ($\varepsilon(Na^+,ClO_4^-)$, $\varepsilon(NpO_2^+,ClO_4^-)$ and $\varepsilon(Na^+,CO_3^{-2})$ values are tabulated in the appendix B); but it is not in accord with the $\Delta\varepsilon_0$ value fitted form Kim's et al. K_{s1} determinations at I= 0.1 to 3 M (see the table and the appendix A). $\varepsilon(NpO_2^+,ClO_4^-) = 0.19 \pm 0.02$ to at least 0.48 ± 0.10 was proposed by this group of authors

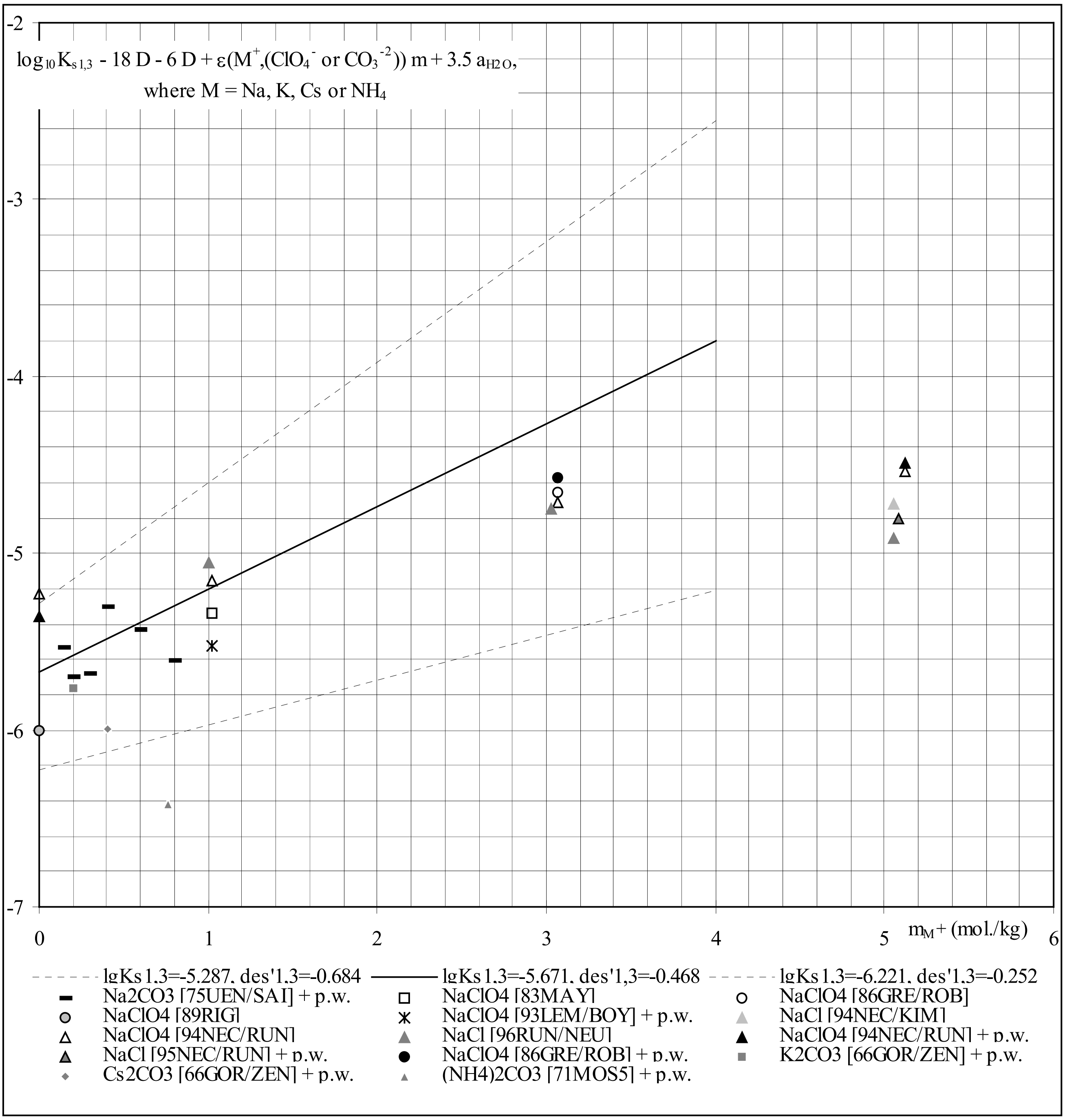


Figure J: **Comparison of $MNpO_2CO_{3(s)}.xH_2O + 2\ CO_3^{-2} \Leftrightarrow M^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O$ equilibrium constant**, $K_{s1,3}$, directly measured for M = Na K, Cs or NH_4 at different ionic strengths, in chemical conditions where $NpO_2(CO_3)_3^{5-}$ contribution to the solubility is high enough ($\log_{10}[CO_3^{-2}]$ > about-2). $\log_{10}K_{s1,3}$ is corrected for Debye-Hückel term, D (see the appendix B), for water activity (a_{H2O}) and for $\varepsilon((Na^+\ K^+\ Cs^+ \text{ or } NH_4^+),(ClO_4^- \text{ or } CO_3^{-2}))$, in this way the theoretical line calculated with the SIT formula is the same for $NaClO_4$ and Na_2CO_3 aqueous solutions. lgKs1,3 = $\mathbf{\log_{10}K_{s1,3}° = -5.67_1 \pm 0.61_2}$ = $\log_{10}(K_{s1}°\ \beta_3°) = \log_{10}(K_{s1}°\ k_1°\ k_3°\ k_2°)$, and $\mathbf{\Delta\varepsilon'_{s1,3} = -0.46_8 \pm 0.21_6}$ **kg.mol.$^{-1}$** = des'1,3 = $\varepsilon(Na^+,NpO_2(CO_3)_3^{-5}) - 2\ \varepsilon(Na^+,CO_3^{-2})$. The scattering of the published data is mainly due to solid phase transformation, for this reason, SIT regression was not used (see the text). The lines are calculated (only for Na^+ media) with the data selected by this review for $k_1°$ (figure A), $k_2°$ (figure B), for $k_3°$ and $\varepsilon(Na^+,NpO_2(CO_3)_2^{3-})$ (figure C), $K_{s1}°$ (figure G), and with ε auxiliary data (Appendix B). The solid line corresponds to freshly precipitated hydrated compound, where x = 3.5 is the most probable value, while the dashed lines give an idea of uncertainty including aged compound, possibly dehydrated. [93LEM/BOY] determination was at 30°C while the other ones are at room temperature. +pw means as re-evaluated by this review.

(or calculated by this review from their data): these numerical values are conflicting, and they did not notice this inconsistency (the value used by this review is $\varepsilon(NpO_2^+,ClO_4^-) = 0.25 \pm 0.05$). The same type of inconsistency was found by this review for their K_{s2} determinations. This confirms the appreciation of this review that suspected systematic error in the glass electrode calibration, possibly due to incorrect junction potential estimation. For this reason, this review did not use the experimental data proposed by that group of authors, for ionic strength corrections. The last paper from this group of authors received by this review confirmed this opinion: there is still an inunderstood problem in the calibration procedure of their glass electrode: there is not enough information to decide whether pH measurements from this laboratory were

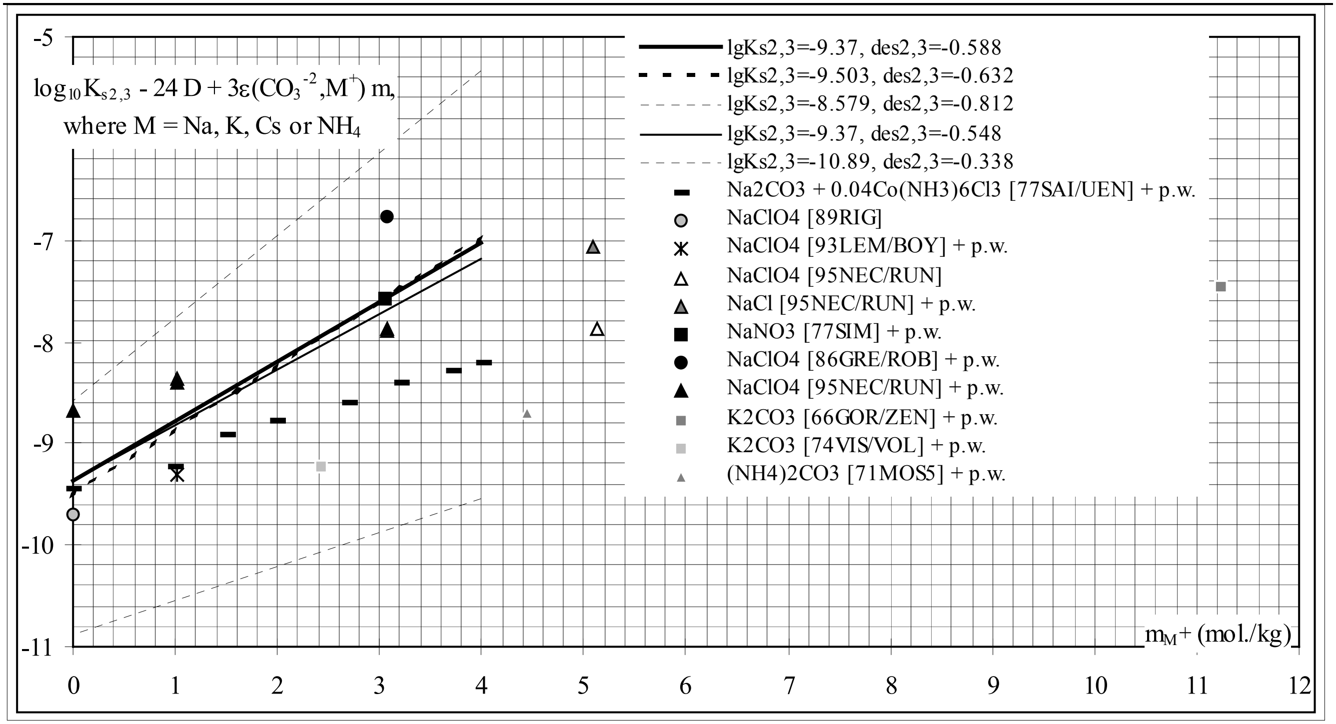


Figure K: Comparison of $M_3NpO_2(CO_3)_{2(s)}.xH_2O$ + 2 CO_3^{-2} ⇔ 3 M^+ + $NpO_2(CO_3)_3^{5-}$ + x H_2O equilibrium constant, $K_{s2,3}$, directly measured for M = Na K, Cs or NH_4 at different ionic strengths. x is unknown. $\log_{10}K_{s2,3}$ is corrected for Debye-Hückel term, D (see the appendix B), for water activity (a_{H2O}) and for ε((Na^+ K^+ Cs^+ or NH_4^+),(ClO_4^- or CO_3^{-2})), in this way the theoretical line calculated with the SIT formula is the same for $NaClO_4$ and Na_2CO_3 aqueous solutions. The scattering of the published data is mainly due to solid phase transformation, for this reason, SIT regression was not used (see the text). The lines are calculated (only for Na^+ media) with the $K_{s2,3}$ value in 3 M $NaNO_3$ aqueous solution as calculated (and selected) by this review from the publication [77SIM], with ε(Na^+,$NpO_2(CO_3)_2^{3-}$) (figure C), and with ε auxiliary data (Appendix B), assuming x = 0 (thick line), which lead to the selected value lgKs2,3 = **$\log_{10}K_{s2,3}°$ = -9.37 ± 2.31_1**. Setting x = 3.5 (arbitrary value) would have change the $K_{s2,3}°$ selected value by much less than the uncertainty (thick dashed line). These lines correspond to freshly precipitated hydrated compound. The other solid line is calculated for $NaClO_4$ aqueous solutions by using des'2,3 = ε(Na^+,$NpO_2(CO_3)_3^{-5}$) - ε(Na^+,CO_3^{-2}) = **$\Delta\varepsilon'_{s2,3}$ = -0.54_8 ± 0.21_0 kg.mol.$^{-1}$**, where the dashed lines give an idea of uncertainty including aged compound, possibly dehydrated. [93LEM/BOY] determination was at 30°C while the other ones are at room temperature. +pw means as re-evaluated by this review.

incorrect, or whether the present review must change some of its auxiliary data (see the discussion of the [96FAN/NEC] publication in the appendix A).

Lemire and Boyer [93LEM/BOY] used published results to choose pH and carbonate chemical conditions where experimental data needed for each soluble complex at 30 to 75°C, should be obtained. Unfortunately they got scattered data. The authors had difficulty to deduced equilibrium constants by curve fitting on their experimental data, and they attributed this problem to solid phase transformation. This was confirmed by x-ray analysis of their solids after liquid-solid equilibration. This observation is of the same type as Vitorge's ones [84VIT], and recently [86RUN/NEU] the x-ray pattern for a $NaNpO_2CO_{3(s)}$ hydrated compound was again published: this review finds that the rays are quite broads, they overlaps (which is not the case for the $Na_3NpO_2(CO_3)_{2(s)}$ diffraction pattern shown in the same publication) which is in accord with Lemire and Boyer [93LEM/BOY], and Vitorge et al. [84VIT, 86GRE/ROB and 89RIG] experimental observations, while Kim et al. claimed (in the publication cited above) that they had not this problem; but they possibly characterised their compounds prior to solubility experiments, and not after solid-liquid equilibration. Lemire and Boyer qualitatively discussed their observations, and using published information on these solids, came to the conclusion, that two $NaNpO_2CO_{3(s)}$ hydrated compounds had been identified, and was certainly formed in the course of their experiments. This solid phase transformation had been proposed to correspond to change in the number of water molecules precipitating with the solid. 3.5 water molecules were assumed to be in the $NaNpO_2CO_{3(s)}$ hydrated compound, by Volkov et al. This is certainly correct, but needs further confirmation. This review still used this number of water molecule for ionic strength corrections (this contribution is anyhow no more than the uncertainty). The lost of (possibly 0.5) water molecule was observed at 30°C. When reinterpreting (graphically) the data of this publication [93LEM/BOY] to extract complexing constants (see above the discussion on the Np(V) carbonate aqueous species, and the appendix A) this review had to make (independently) the same type of qualitative interpretation of solid phase transformation, as the authors did.

This review then followed this conclusion: in the published solubility data the $NaNpO_2CO_{3(s)}$ hydrated compounds were ageing, solid phase transformation is suspected just above room temperature, and it is not clear whether this is a kinetic problem or whether (at least) two solubility products should be selected. On the other hand, the corresponding scattering of the solubility product determinations, is not so important (about 1 $\log_{10}$ unit) and can explain other experimental observations (see the discussion of the [84VIT and 93LEM/BOY] publications in the appendix A). This review did not then fit $\Delta\varepsilon_{s1}$ value on published experimental determinations of solubility products, K_{s1}, at different ionic strengths (or of $K_{s1,i}$ = K_{s1} β_i), since the influence of this parameter is not much more than the one due to the above solid phase transformation.

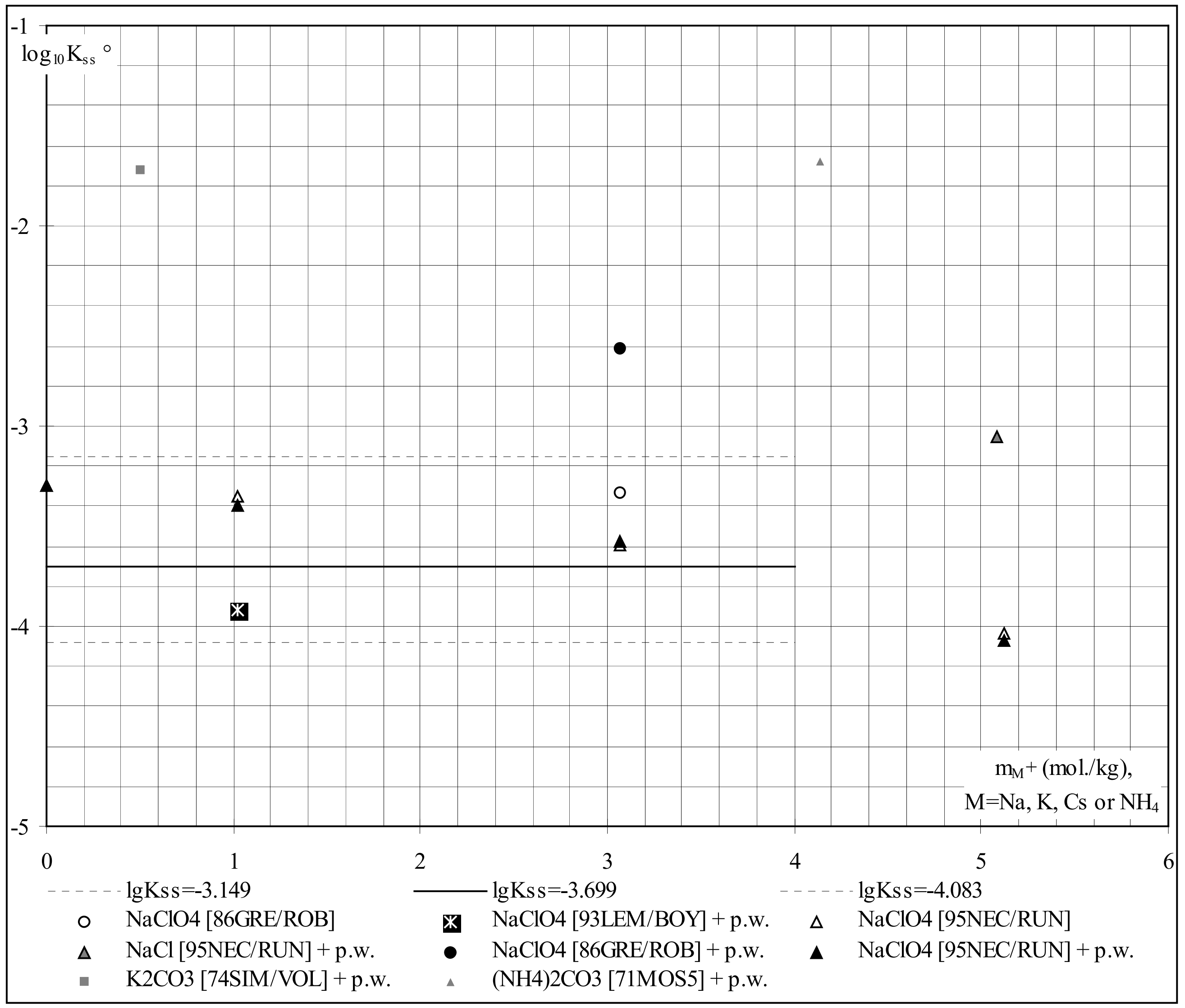


Figure L: Comparison of $M_3NpO_2(CO_3)_{2(s)}.xH_2O + (y\text{-}x)\ H_2O \Leftrightarrow MNpO_2CO_{3(s)}.yH_2O + CO_3^{-2} + 2\ Na^+$ equilibrium constant, K_{ss}, extrapolated to I=0 by using the SIT and the auxiliary ε values of the appendix B. M = Na K, Cs or NH_4. x and y are unknown and the scattering of the published data is mainly due to solid phase transformation (see the text). $K_{ss} = K_{s2} / K_{s1} = K_{s2,3} / K_{s1,3}$ values are deduced from those of the figures J and K with the same ionic strength corrections which leads to the standard value $\mathbf{log_{10}K_{ss}° = -3.69_9 \pm 2.39_1}$.

The $\Delta\varepsilon_{s1,i}$ values are known independently (see above). They were then used to compare the $K_{s1,i}$ (i = 0, 1, 2 and 3) determination (see the figures) and to propose the following standard values

$log_{10}K_{s1}°$ = -10.95 for freshly precipitated $NaNpO_2CO_{3(s)}$ hydrated compound,
$log_{10}K_{s1}°$ = -11.53 for aged or less hydrated $NaNpO_2CO_{3(s)}$ compound,
$log_{10}K_{s1}°$ = -11.15 ± 0.59 overlap the above values

where hydrated $NaNpO_2CO_{3(s)}$ is assumed to be $NaNpO_2CO_{3(s)},3.5H_2O$; but this should be confirmed. These numbers overlap all published data; but, as for the Np(V) carbonate aqueous species, the Kim's et al. solubility data were first extrapolated to zero ionic strength alone to minimise the possible systematic deviation discussed above, and only this value at I = 0 was used by this review from Kim's et al. data.

According to this interpretation, the smallest solubility product value was obtained at 30°C [93LEM/BOY] where a new solid phase is supposed to appear. The next value is obtained by the work that probably used the longest equilibration time at room temperature [86GRE/VIT], then Maya's value [83MAY] who probably performed the quickest experiment. All this makes sense: experimental description, x-ray and solubility results are consistent with a freshly Maya's precipitated $NaNpO_2CO_{3(s)}$ compound, while Vitorge's et al. one was aged, and Lemire and Boyer's one had started to be transformed into a more stable phase, possibly partially dehydrated at 30°C. Temperature influence on solubility observed by Lemire and Boyer was then not used by this review to estimate ΔH_r for reaction involving solid compounds, since solid phase transition contribution to ΔH could certainly not be neglected. Anyhow these solubility product variations between two consecutive values, are of the order of magnitude of the uncertainty. Following the evaluation of this review that considered his data only at zero ionic strength, Kim's and co-authors' determination would correspond to the more soluble compound which is quite surprising and certainly wrong: $K_{s1,1}$ does not depend on the $[CO_3^{-2}]$ and then on pH calibration (i.e. on the systematic deviations suspected in that work by this review), its direct determination was found to be the same as Maya's one (at I = 1M), while at I = 3M, it is less than the value measured in the [86GRE/VIT] work.

This review compared the published solubility product determinations (figure G) by subtracting the Debye-Hückel contribution; which give the same figure as usually shown for extrapolation to zero ionic strength by this review. As explained above, no linear regression was performed for this figure, where the slope was calculated from ε values. Similar plots were performed by this review (figures G to L) for the

$$NaNpO_2CO_{3(s)}.xH_2O \Leftrightarrow Na^+ + NpO_2CO_3^- + x\ H_2O$$

$$NaNpO_2CO_{3(s)}.xH_2O + CO_3^{-2} \Leftrightarrow Na^+ + NpO_2(CO_3)_2^{3-} + x\ H_2O$$

$$NaNpO_2CO_{3(s)}.xH_2O + 2\ CO_3^{-2} \Leftrightarrow Na^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O$$

equilibria to visualise the solubility product determinations in chemical conditions where aqueous Np(V) carbonate complexes predominate. Measurements in other media were also added to estimate solubility products for other alkaline cations.

$Na_3NpO_2(CO_3)_{2(s)}$

The same type of observation can be made for $Na_3NpO_2(CO_3)_{2(s)}$ hydrated compounds and corresponding solubility products; but it is even not clear if there is a true solid phase transformation (when increasing temperature) between solids with the same stoichiometry and possibly loosing water, or whether there is any solid phase with intermediary stoichiometry between $NaNpO_2CO_{3(s)}$ and $Na_3NpO_2(CO_3)_{2(s)}$ (see the discussion of the [93LEM/BOY] publication in the appendix A). The same treatment was performed for the

$$Na_3NpO_2(CO_3)_{2(s)}.xH_2O + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ Na^+ + x\ H_2O$$

equilibrium (figure). The results are in the table; but the number of water molecules is not known. The $K_{s2,3}$ value proposed by this review is the one determined from Simakin's data as interpreted by this review (see the appendix A), because it is the only author who prepared this solid to study the above equilibrium. Its value at I = 3 M, is higher than the mean values estimated from Vitorge et al. data [85COM, 85KIM, 86GRE/ROB and 89RIG], which is clearly due to solid evolution: the value selected by this review corresponds then to freshly precipitated compound. The value determined from Kim's et al data at I = 3M is even lower; but is in accord with Simakin's one when extrapolated to zero ionic strength, which could be attributed to systematic deviation discussed above for Kim's et al. data at high ionic strength. Lemire and Boyer's data at 30°C and some of Vitorge's et al. at 25°C are even lower, certainly because a new phase was precipitating (see the discussion of the [93LEM/BOY] publication in the appendix A).

The transformation of $Na_3NpO_2(CO_3)_{2(s)}$ into $NaNpO_2CO_{3(s)}$ is controlled by the

$$Na_3NpO_2(CO_3)_{2(s)}.xH_2O + (y - x)\ H_2O \Leftrightarrow NaNpO_2CO_{3(s)}.yH_2O + CO_3^{-2} + 2\ Na^+$$

equilibrium whose constant can be deduced from the two solubility products or directly measured (figure L).

Tables

Np(V) carbonate complexing constants extrapolated to zero ionic strength, and SIT coefficients

$k_i = [NpO_2(CO_3)_i^{1-2i}] /([NpO_2(CO_3)_{i-1}^{3-2i}] [CO_3^{-2}])$. $K_{sj} = [Na^+]^{1-2j} [NpO_2^+] [CO_3^{-2}]^j$ is the solubility product of the $Na_{1-2j}NpO_2(CO_3)_j.x_jH_2O$ compound where x_j values are not clearly established (see the text): $x_1 = 3.5$ and $x_2 = 0$ were used. $\varepsilon_0 = \varepsilon(NpO_2^+,ClO_4^-)$, $\varepsilon_i = \varepsilon(Na^+,NpO_2(CO_3)_i^{1-2i})$. $\Delta\varepsilon_i = \varepsilon_i - \varepsilon_{i-1} - \varepsilon(Na^+,CO_3^{-2})$ corresponds to k_i. Published data selected by this review are bolded [pw], the other [pw] data are weighted linear regression on the same data. References [91KIM/KLE] [94NEC/RUN] [95FAN/NEC, 95NEC/FAN] [95NEC/RUN] [96RUN/NEU] are from the same group of authors. The data of reference [95NOV/ROB] are as cited in [96RUN/NEU] (it was not available to the reviewers), most of them are not in accord with the one selected by this review.

Ref.	$\log_{10}k_1°$	$\log_{10}k_2°$	$\log_{10}k_3°$	$\log_{10}K_{s1}°$	$\log_{10}K_{s2,3}°$
[83MAY, 86GRE/ROB]	4.96_7	1.49_1	-1.20_0	-10.96_1	
89RIG][2]	$4.79_8 \pm 0.11_3$	$1.50_1 \pm 0.01_2$	$-0.88_2 \pm 0.00_1$		
89RIG][1]			$-1.16_7 \pm 0.17_0$		
[90NIT/STA][3]	4.69 ±0.13				
[91KIM/KLE]	5.04 ±0.06	1.55 ±0.11	-0.86 ±0.19	-10.96 ±0.05	
[94NEC/RUN]	4.81 ±0.15	1.74 ±0.27	-1.01 ±0.25	-11.00 ±0.07	
[94NEC/RUN][2]	$5.02_9 \pm 0.10_1$		-0.94_5	$-10.94_3 \pm 0.11_5$	-8.61_0
[94NEC/RUN][1]	$4.96_7 \pm 0.13_5$	$1.60_0 \pm 0.08_3$	-0.94_5	$-10.95_0 \pm 0.10_5$	-8.66_5
[94NEC/RUN][4]	$5.06_6 \pm 0.12_4$			$-10.94_2 \pm 0.07_3$	$-8.41_8 \pm 0.44_5$
[94NEC/RUN][5]	$5.03_1 \pm 0.20_1$	$1.56_6 \pm 0.11_0$	$-0.93_8 \pm 0.01_7$	$-10.94_6 \pm 0.06_8$	$-8.60_5 \pm 0.93_7$
[94NEC/RUN][6]					$-8.53_7 \pm 0.61_3$
[95FAN/NEC, 95NEC/FAN][7]	5.03 ±0.06	1.44 ±0.15	-1.10 ±0.39	-10.94 ±0.08	-8.95 ±0.39
[95NEC/RUN]				-11.00 ±0.07	
[96RUN/NEU][7]	5.06	1.43	-1.07	-11.14	-8.90
[95NOV/ROB][7,3]	5.39	0.42	-0.62		
[pw][8]	**$4.94_8 \pm 0.18$(9)**	**$1.56_9 \pm 0.09_7$**	**$-1.03_8 \pm 0.12_3$**	**-11.15 ±0.59**	**$-9.37 \pm 2.31_1$**
[pw]	4.92 ±0.03	1.58 ±0.09	-1.04 ±0.12		

Ref.	$-\Delta\varepsilon_1$	$-\Delta\varepsilon_2$	$-\Delta\varepsilon_3$	ε_1	ε_2	ε_3
[83MAY, 86GRE/ROB]	0.39_1	0.11_7	0.21_9	-0.22_1	-0.41_8	-0.71_7
89RIG][2]	$0.32_8 \pm 0.08_3$	$0.03_5 \pm 0.00_9$	$0.25_9 \pm 0.00_1$	$-0.15_8 \pm 0.10_2$	$-0.27_3 \pm 0.11_4$	$-0.61_2 \pm 0.13_3$
89RIG][1]			$0.15_7 \pm 0.14_4$			
[90NIT/STA][3]	-0.43 ±0.18			-0.26 ±0.19		
[91KIM/KLE]	0.19 ±0.03	0.09 ±0.05	0.11 ±0.08	-0.02 ±0.07	-0.19 ±0.10	-0.38 ±0.14
[94NEC/RUN]	0.30 0±.04	0.05 ±0.07	0.11 ±0.07	-0.13 ±0.07	-0.26 ±0.11	-0.45 ±0.15
[94NEC/RUN][2]	$0.21_6 \pm 0.05_4$		0.17_5	$-0.04_6 \pm 0.07_9$		-0.38_1
[94NEC/RUN][1]	$0.24_1 \pm 0.07_2$	$0.08_7 \pm 0.04_4$	0.17_5	$-0.07_1 \pm 0.09_3$	$-0.23_8 \pm 0.11_5$	-0.49_3
[94NEC/RUN][4]	$0.17_8 \pm 0.04_1$			$-0.00_8 \pm 0.07_1$		
[94NEC/RUN][5]	$0.17_6 \pm 0.06_7$	$0.12_2 \pm 0.03_6$	$0.17_1 \pm 0.00_5$	$-0.00_6 \pm 0.08_8$	$-0.20_7 \pm 0.10_9$	$-0.45_8 \pm 0.12_8$
[95FAN/NEC, 95NEC/FAN][7]				0.06	0.12 ±0.30	1.29 ±0.54
[96RUN/NEU][7]	0.05 ±0.09	-0.13 ±0.30	-0.55 ±0.81	0.06 ±0.08	0.11 ±0.29	0.58 ±0.76
[95NOV/ROB][7,3]	0.05 ±0.12	-0.04 ±0.50	-0.73 ±1.01	0.09 ±0.08	0.05 ±0.49	0.70 ±0.88
[pw][8]	**$0.39_6 \pm 0.15_5$**	**$0.08_6 \pm 0.05_2$**	**$0.15_6 \pm 0.07_6$**	**$-0.22_6 \pm 0.16_6$**	**$-0.39_2 \pm 0.18_1$**	**$-0.62_8 \pm 0.20_8$**
[pw]	0.39 ±0.03	0.05 ±0.09	0.16 ±0.07	-0.22 ±0.06	-0.35 ±0.11	-0.59 ±0.13

[1] Experimental data were re-evaluated by this review, and[2]. [2] Extrapolation to I=0 was performed by this review. [3] Including data published by other authors. [4] Including data in5 M $NaClO_4$ and[2 and 3]. [5] = [4]and[1]. [6] = [5] including data in 5 M NaCl. [7] Pitzer's equation was used by the author for extrapolation to I = 0, this review calculated ε values from Pitzer's parameters, the uncertainty is estimated as the difference in ε values between 0.5 and 4 kg.mol.$^{-1}$. Unbelievable values are obtained in this way for ε_i, possibly because the authors originally fitted Pitzer's parameters for mixed electrolyte that was set to 0 by this review to compare with $NaClO_4$ pure electrolyte data. [8] Data proposed by this review. [9] 1.96 σ is 0.04_9, but uncertainty has been increased (see text).

Published equilibrium constants.

In the first $\log_{10}K$ column, values of stability constants are tabulated as reported in the publication (see the column reference), or calculated from equilibrium constant values reported in the publication (thermodynamic cycle). In the next $\log_{10}K$ column is tabulated recalculation by this review (see the foot notes) as explained in the appendix A. The values proposed by this review at zero ionic strength are in a separate table. They were calculated from the values at various ionic strengths for which a foot note indicates, that they were used by this review for extrapolation to zero ionic strength (see the text and the appendix B). The other values were then not used by this review (for the reasons explained in the appendix A) to select thermodynamic data. Literature compilations are not tabulated. Published extrapolations to zero ionic strength are tabulated elsewhere. TBA is the tetrabutylammonium cation.

medium	t(°C)	method	$\log_{10}K$	$\log_{10}K$	reference
$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$					
0.016 M HCO_3^- + ?	?	sp	5.5 ± 0.5		[81BIL][ak]
0.1 M $NaClO_4$	25	dis	4.13 ± 0.03	3.80[d] ± 0.36	[85BID/TAN]
0.1 M $NaClO_4$	23	sp	4.34 ± 0.11	**4.56**[de] ± 0.67	[90NIT/STAN]
0.1 M $NaClO_4$	25	sol	4.58 ± 0.04	4.51[d] ± 0.22	[91KIM/KLE][n]
0.1 M $NaClO_4$	25	sol	4.52 ± 0.02		[94MEI][n]
0.1 M $NaClO_4$	25	sp	4.38 ± 0.04		[94NEC/KIM][n]
0.1 M $TBANO_3$	25	sp	4.12 ± 0.17		[96CLA/CON2]
0.1 M $TBANO_3$	70	sp	3.75 ± 0.16		[96CLA/CON2]
0.1 M NaCl	23	sol	4.68		[96RUN/NEU][ln]
0.1 M NaCl	23	sol	4.8 ±		[96RUN/NEU][n]
0.5 M $NaClO_4$	22	sp	4.3 ± 0.1	**4.41**[de] ±0.1	[89RIG]
0.5 M $NaClO_4$	75	sol		4.8 ± 0.28	[93LEM/BOY][dk]
1 M $NaClO_4$	25	sol	4.49 ± 0.06	**4.57**[de] ± 0.35	[83MAY]
1 M $NaClO_4$	25	sol	4.6 ± 0.1		[83MAY][g]
1 M $NaClO_4$	25	dis	4.14 ± 0.01	4.14[d] ± 0.5	[85INO/TOC]
1 M $NaClO_4$	22	sp	4.3 ± 0.2		[89RIG]
1 M $NaClO_4$	25	sol	4.50 ± 0.04	4.48[d] ± 0.36	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol	4.7 ± 0.1	4.77[dk] ± 0.51	[93LEM/BOY]
1 M $NaClO_4$	50	sol	5.6 ± 0.2	5.7[dk] ± 0.54	[93LEM/BOY]
1 M $NaClO_4$	75	sol	5.80 ± 0.58	5.2[dk] ± 0.54	[93LEM/BOY]
1 M NaCl	23	sol	4.32 ± 0.07		[96RUN/NEU][ln]
2 M $NaClO_4$	22	sp	4.6 ± 0.3		[89RIG]
3 M $NaClO_4$	22	sol	5.09 ± 0.57	**5.25**[de] ± 0.29	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	4.76 ± 0.04	4.77[d] ± 0.43	[91KIM/KLE][n]
3 M NaCl	23	sol	4.3 ± 0.1		[96RUN/NEU][n]
3 M NaCl	23	sp	4.67 ± 0.07		[96RUN/NEU][ln]
5 M $NaClO_4$	25	sol	5.00 ± 0.05	4.92[d] ± 0.81	[94NEC/KIM][n]
5 M NaCl	25	sol	5.70[m]	4.68	[94NEC/KIM][n]
5 M NaCl	23	sol	4.71 ± 0.04		[96RUN/NEU][ln]
5 M NaCl	23	sp	4.72 ± 0.13		[96RUN/NEU][ln]
$NpO_2^+ + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$					
0.1 M $NaClO_4$	25	sol	6.60 ± 0.07	6.59[d] ± 0.44	[91KIM/KLE][n]
0.1 M $NaClO_4$	25	sp	6.4 ± 0.3		[94NEC/KIM][n]
0.1 M $TBANO_3$	25	sp	6.10 ± 0.25		[96CLA/CON2]
0.1 M $TBANO_3$	70	sp	5.75 ± 0.25		[96CLA/CON2]
0.2 M $NaClO_4$	25	dis	7.06 ± 0.05	7.22[d] ± 0.78	[85BID/TAN]
0.5 M $NaClO_4$	22	sp	6.4 ± 0.2		[89RIG]
0.5 M $NaClO_4$	75	sol		7.20 ± 0.36	[93LEM/BOY][dk]
1 M $NaClO_4$	25	sol	7.11 ± 0.07	7.03[d] ± 0.24	[83MAY]
1 M $NaClO_4$	25	sol	7.1 ± 0.1		[83MAY][g]
1 M $NaClO_4$	25	dis	6.78 ± 0.01	6.78[d] ± 0.5	[85INO/TOC]
1 M $NaClO_4$	22	sp	6.7 ± 0.3		[89RIG]
1 M $NaClO_4$	25	sol	6.96 ± 0.06	6.97[d] ± 0.62	[91KIM/KLE]
1 M $NaClO_4$	30	sol	7.0 ± 0.1	7.47[dk] ± 0.54	[93LEM/BOY]
1 M $NaClO_4$	50	sol	6.9 ± 0.3	8.80[dk] ± 0.57	[93LEM/BOY]
1 M $NaClO_4$	75	sol	8.80 ± 1.62	7.30[dk] ± 0.61	[93LEM/BOY]
1 M NaCl	23	sol	6.49 ± 0.09		[96RUN/NEU][ln]
2 M $NaClO_4$	22	sp	7.1 ± 0.4		[89RIG]
3 M $NaClO_4$	22	sol	8.15 ± 0.43	8.15 ± 0.46[d]	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	7.69 ± 0.07	7.69[d] ± 0.83	[91KIM/KLE][n]
3 M NaCl	23	sol	7.1 ± 0.2		[96RUN/NEU][n]

medium	t(°C)	method	$\log_{10}K$	$\log_{10}K$	reference
5 M $NaClO_4$	25	sol	8.29 ± 0.09	8.32[d] ± 1.46	[94NEC/KIM][n]
5 M NaCl	25	sol	8.25[m]	7.23	[94NEC/KIM][n]
5 M NaCl	23	sol	7.54 ± 0.05		[96RUN/NEU][ln]
5 M NaCl	23	sp	7.63 ± 0.19		[96RUN/NEU][ln]
$NpO_2CO_3^- + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$					
0.008 M CO_3^{-2} + ?	?	sp		2.5 ± 0.5	[81BIL][ak]
0.1 M HCO_3^-	?	dis		2.3 ± 1.0	[79MOS/POZ][ak]
0.1 M $NaClO_4$	25	sol	2.02 ± 0.08	2.08[d] ± 0.22	[91KIM/KLE][n]
0.1 M $NaClO_4$	25	sp	2.02 ± 0.3		[94NEC/KIM][n]
0.1 M $TBANO_3$	25	sp	1.99 ± 0.2		[96CLA/CON2]
0.1 M $TBANO_3$	70	sp	1.99 ± 0.2		[96CLA/CON2]
0.04 M Na_2CO_3	22	sp		1.4 ± 0.3	[89RIG][d]
0.05 M Na_2CO_3		sol		2.08 ± 0.29	[75UEN/SAI][ak]
0.2 M $NaClO_4$	25	dis	2.93	3.42[d] ± 1.0	[85BID/TAN]
0.16 M CO_3^{-2} + ?	?	sp		1.4 ± 1	[81BIL][ak]
0.5 M $NaClO_4$	22	sp	2.23 ± 0.07		[89RIG]
0.5 M $NaClO_4$	75	sol		2.40 ± 0.36	[93LEM/BOY][dk]
1 M $NaClO_4$	25	sol	2.62 ± 0.09	**2.45**[d,e] ± 0.26	[83MAY]
1 M $NaClO_4$	25	sol	2.5 ± 0.14		[83MAY][g]
1 M $NaClO_4$	25	dis	2.64 ± 0.02	2.64[d] ± 0.70	[85INO/TOC]
1 M $NaClO_4$	22	sp	2.38 ± 0.07		[89RIG]
1 M $NaClO_4$	25	sol	2.46 ± 0.08	2.49[d] ± 0.36	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol	2.3 ± 0.14	2.7[dk] ± 0.22	[93LEM/BOY]
1 M $NaClO_4$	50	sol	1.3 ± 0.36	3.1[dk] ± 0.18	[93LEM/BOY]
1 M $NaClO_4$	75	sol	3 ± 1.52	2.1[dk] ± 0.28	[93LEM/BOY]
1 M KCl	75	sol		2.2[dk] ± 0.4	[93LEM/BOY]
1 M NaCl	23	sol	2.17 ± 0.13		[96RUN/NEU][ln]
2 M $NaClO_4$	22	sp	2.54 ± 0.07		[89RIG]
3 M $NaClO_4$	22	sol	3.06 ± 0.21[d]	**2.90**[de] ± 0.17	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	2.93 ± 0.08	2.93[d] ± 0.46	[91KIM/KLE][n]
3 M NaCl	23	sol	2.8 ± 0.2		[96RUN/NEU][n]
5 M $NaClO_4$	25	sol	3.29 ± 0.10	3.40[d] ± 0.70	[94NEC/KIM][n]
5 M NaCl	25	sol	2.55		[94NEC/KIM][n]
5 M NaCl	23	sol	2.83 ± 0.06		[96RUN/NEU][ln]
5 M NaCl	23	sp	2.91 ± 0.20		[96RUN/NEU][ln]
$NpO_2^+ + 3\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$					
0.5 M $NaClO_4$	75	sol		8.55 ± 0.56	[93LEM/BOY][dk]
1 M $NaClO_4$	22	sp	8.5 ± 0.4		[89RIG]
1 M $NaClO_4$	25	sol	8.53 ± 0.09	8.52[d] ± 0.41	[83MAY]
1 M $NaClO_4$	25	sol	8.5 ± 0.1		[83MAY][g]
1 M $NaClO_4$	25	sol	8.67 ± 0.09	8.68[d] ± 0.88	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol		8.97± 0.58	[93LEM/BOY][dk]
1 M $NaClO_4$	50	sol	8.6 ± 0.3	10.30[dk] ± 0.66	[93LEM/BOY]
1 M $NaClO_4$	75	sol	10.10 ± 1.42	8.90[dk] ± 0.61	[93LEM/BOY]
1 M NaCl	23	sol	8.43 ± 0.06		[96RUN/NEU][ln]
2 M $NaClO_4$	22	sp	9.6 ± 0.5		[89RIG]
3 M $NaClO_4$	22	sol	10.46 ± 0.38[d]	10.64[d] ± 0.37	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	10.30 ± 0.10	10.30[d] ± 0.86	[91KIM/KLE][n]
3 M NaCl	23	sol	9.2 ± 0.2		[96RUN/NEU][n]
5 M $NaClO_4$	25	sol	11.47 ± 0.08	11.52[d] ± 2.00	[94NEC/KIM][n]
5 M NaCl	25	sol	10.75[m]	9.73	[94NEC/KIM][n]
5 M NaCl	23	sol	9.63 ± 0.05		[96RUN/NEU][ln]
$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$					
0.07 M Na_2CO_3		sol		0.28 ± 0.23	[75UEN/SAI][ak]
0.1 M Na_2CO_3		sol		0.56 ± 0.23	[75UEN/SAI][ak]
0.15 M Na_2CO_3		sol		0.99 ± 0.23	[75UEN/SAI][ak]
0.16 M CO_3^{-2} + ?		sp		1.4 ± 1	[81BIL][ak]
0.17 M Na_2CO_3	22	sp		0.90 ± 0.2	[89RIG][d]
0.2 M Na_2CO_3		sol		0.96 ± 0.23	[75UEN/SAI][ak]
0.5 M $NaClO_4$	22	sp	1.30 ± 0.07	**1.13**[de] ± 0.2	[89RIG]
0.5 M $NaClO_4$	75	sol		1.35 ± 0.42	[93LEM/BOY][dk]

medium	t(°C)	method	$\log_{10}K$	$\log_{10}K$	reference
0.3 M Na_2CO_3		sol		1.14 ± 0.23	[75UEN/SAI][ak]
1 M $NaClO_4$	25	sol	1.42 ± 0.11	**1.50**[de] ± 0.36	[83MAY]
1 M $NaClO_4$	25	sol		1.4 ± 0.14	[83MAY][g]
1 M $NaClO_4$	22	sp	1.60 ± 0.07	**1.48**[de] ± 0.2	[89RIG]
1 M $NaClO_4$	25	sol	1.71 ± 0.12	1.71[d] ± 0.13	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol		1.5[dk] ± 0.22	[93LEM/BOY]
1 M $NaClO_4$	50	sol	1.7 ± 0.42	1.5[dk] ± 0.34	[93LEM/BOY]
1 M $NaClO_4$	75	sol	1.3 ± 1.41	1.6[dk] ± 0.28	[93LEM/BOY]
1 M KCl	75	sol		2.5[dk] ± 0.45	[93LEM/BOY]
1 M NaCl	23	sol	2.06 ± 0.13		[96RUN/NEU][ln]
2 M $NaClO_4$	22	sp	2.05 ± 0.07	**1.96**[de] ± 0.2	[89RIG]
3 M $NaClO_4$	22	sp	2.9 ± 0.2		[89RIG]
3 M $NaClO_4$	22	sol	2.31 ± 0.14	**2.49**[de] ± 0.07	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	2.61 ± 0.12	2.61[d] ± 0.50	[91KIM/KLE][n]
3 M NaCl	23	sol	2.1 ± 0.2		[96RUN/NEU][n]
5 M $NaClO_4$	25	sol	3.18 ± 0.10	3.20[d] ± 0.80	[94NEC/KIM][n]
5 M NaCl	25	sol	2.50		[94NEC/KIM][n]
5 M NaCl	23	sol	2.09 ± 0.07		[96RUN/NEU][ln]
$NaNpO_2CO_{3(s)}.xH_2O \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{-2} + x\ H_2O$[x]					
0.1 M $NaClO_4$	25	sol	-10.22 ± 0.02		[94MEI][n]
0.1 M $NaClO_4$	25	sol	-10.28 ± 0.04	-10.29[d] ± 0.16	[91KIM/KLE][n]
0.1 M NaCl	23	sol	-10.4 ± 0.2		[96RUN/NEU][n]
0.5 M $NaClO_4$	75	sol		-9.80 ± 0.2	[93LEM/BOY][dk]
1 M $NaClO_4$	25	sol	-10.14 ± 0.04	-10.12[d]± 0.35	[83MAY]
1 M $NaClO_4$	25	sol	-10.12 ± 0.04		[83MAY][g]
1 M $NaClO_4$	25	sol	-10.10 ± 0.03	-10.10[d] ± 0.36	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol	-10.7 ± 0.1	-10.77[dk] ± 0.5	[93LEM/BOY]
1 M $NaClO_4$	50	sol	-11.0 ± 0.1	-11.1[dk] ± 0.2	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-10.94 ± 0.29	-10.5[dk] ± 0.5	[93LEM/BOY]
1 M NaCl	23	sol	-9.77 ± 0.16		[96RUN/NEU][ln]
3 M $NaClO_4$	22	sol	-10.56 ± 0.34	-10.65[d] ± 0.33	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	-10.45 ± 0.04	-10.45[d] ± 0.42	[91KIM/KLE][n]
3 M NaCl	23	sol	-9.4 ± 0.2		[96RUN/NEU][n]
3 M NaCl	23	sol	-9.61 ± 0.11		[96RUN/NEU][ln]
5 M $NaClO_4$	25	sol	-11.06 ± 0.06	-11.07[d] ± 0.74	[94NEC/KIM][n]
5 M NaCl	25	sol	-9.52[m]	-10.54	[94NEC/KIM][n]
5 M NaCl	25	sol	-9.61 ± 0.11		[95NEC/RUN][mn]
$KNpO_2CO_{3(s)}.xH_2O \Leftrightarrow K^+ + NpO_2^+ + CO_3^{-2} + x\ H_2O$[x]					
diluted?	20	pot		-10.3 ± 2.0	[74VIS/VOL][ak]
1 M KCl	75	sol		-6.7 ± 0.2	[93LEM/BOY][dk]
$NaNpO_2CO_{3(s)}.xH_2O \Leftrightarrow Na^+ + NpO_2CO_3^- + x\ H_2O$[x]					
0.1 M $NaClO_4$	25	sol	-5.70 ± 0.03		[94MEI][n]
0.1 M $NaClO_4$	25	sol	-5.70 ± 0.03	-5.78[d] ± 0.20	[91KIM/KLE][n]
0.1 M NaCl	23	sol	-5.6 ± 0.2		[96RUN/NEU][ln]
0.5 M $NaClO_4$	75	sol		-5.00 ± 0.2	[93LEM/BOY][dk]
1 M $NaClO_4$	25	sol	-5.65 ± 0.07	-5.55[d] ± 0.35	[83MAY]
1 M $NaClO_4$	25	sol	-5.52 ± 0.11		[83MAY][g]
1 M $NaClO_4$	25	sol	5.60 ± 0.05	-5.62[d] ± 0.10	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol	-6 ± 0.14	-6[dk] ± 0.1	[93LEM/BOY]
1 M $NaClO_4$	50	sol	-5.4 ± 0.22	-5.4[dk] ± 0.5	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-5.14 ± 0.51	-5.3[dk] ± 0.2	[93LEM/BOY]
1 M NaCl	23	sol	-5.1 ± 0.2		[96RUN/NEU][n]
1 M NaCl	23	sol	-5.45 ± 0.20		[96RUN/NEU][ln]
3 M $NaClO_4$	22	sol	-5.47 ± 0.42	-5.40[d] ± 0.32	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	-5.69 ± 0.06		[91KIM/KLE][n]
3 M NaCl	23	sol	-5.31 ± 0.15		[96RUN/NEU][n]
5 M $NaClO_4$	25	sol	-6.06 ± 0.09	-6.15[d] ± 0.18	[94NEC/KIM][n]
5 M NaCl	25	sol	-4.84		[94NEC/KIM][n]
5 M NaCl	23	sol	-4.90 ± 0.13		[96RUN/NEU][ln]

medium	t(°C)	method	log$_{10}$K		log$_{10}$K		reference
$KNpO_2CO_{3(s)}.xH_2O \Leftrightarrow K^+ + NpO_2CO_3^- + x\ H_2O$[x]							
Diluted medium?		pot			-10.15		[74VIS/VOL][dk]
1 M KCl	75	sol			-6.7	± 0.2	[93LEM/BOY][dk]
$NaNpO_2CO_{3(s)}.xH_2O + CO_3^{-2} \Leftrightarrow Na^+ + NpO_2(CO_3)_2^{3-} + x\ H_2O$[x]							
0.1 M $NaClO_4$	25	sol	-3.68	± 0.08	-3.70[d]	± 0.39	[91KIM/KLE][n]
0.05 M Na_2CO_3		sol			-3.72	± 0.23	[75UEN/SAI][ak]
0.07 M Na_2CO_3		sol			-3.72	± 0.23	[75UEN/SAI][ak]
0.1 M Na_2CO_3		sol			-3.67	± 0.29	[75UEN/SAI][ak]
0.15 M Na_2CO_3		sol			-3.61	± 0.45	[75UEN/SAI][ak]
0.2 M Na_2CO_3		sol			-2.94	± 0.63	[75UEN/SAI][ak]
0.3 M Na_2CO_3		sol			-2.92	± 0.96	[75UEN/SAI][ak]
1 M $NaClO_4$	25	sol	-3.03	± 0.08	-3.10[d]	± 0.24	[83MAY]
1 M $NaClO_4$	25	sol	-3.02	± 0.11			[83MAY][g]
1 M $NaClO_4$	25	sol	-3.14	± 0.07	-3.13[d]	± 0.36	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol	-3.70	± 0.14	-3.3[dk]	± 0.2	[93LEM/BOY]
1 M $NaClO_4$	50	sol	-4.10	± 0.32	-2.3[dk]	± 0.53	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-2.14	± 1.60	-3.2[dk]	± 0.35	[93LEM/BOY]
1 M NaCl	23	sol	-3.28	± 0.20			[96RUN/NEU][ln]
3 M $NaClO_4$	22	sol	-2.41	± 0.25	-2.50[d]	± 0.33	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	-2.76	± 0.08	-2.76[d]	± 0.46	[91KIM/KLE][n]
3 M NaCl	23	sol	-2.3	± 0.2			[96RUN/NEU][n]
5 M $NaClO_4$	25	sol	-2.77	± 0.11	-2.75[d]	± 0.77	[94NEC/KIM][n]
5 M NaCl	25	sol	-2.29				[94NEC/KIM][n]
5 M NaCl	23	sol	-2.07	± 0.14			[96RUN/NEU][ln]
$KNpO_2CO_{3(s)}.xH_2O + CO_3^{-2} \Leftrightarrow K^+ + NpO_2(CO_3)_2^{3-} + x\ H_2O$[x]							
1 M KCl	75	sol			-4.5	± 0.45	[93LEM/BOY][dk]
$NaNpO_2CO_{3(s)}.xH_2O + 2\ CO_3^{-2} \Leftrightarrow Na^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O$[x]							
0.07 M Na_2CO_3		sol			-3.04	± 1.25	[75UEN/SAI][ak]
0.1 M Na_2CO_3		sol			-2.92	± 0.92	[75UEN/SAI][ak]
0.15 M Na_2CO_3		sol			-2.58	± 0.64	[75UEN/SAI][ak]
0.2 M Na_2CO_3		sol			-1.97	± 0.51	[75UEN/SAI][ak]
0.5 M $NaClO_4$	75	sol			-1.25	± 0.52	[93LEM/BOY][dk]
0.3 M Na_2CO_3		sol			-1.78	± 0.42	[75UEN/SAI][ak]
0.4 M Na_2CO_3		sol			-1.72	± 0.39	[75UEN/SAI][ak]
1 M $NaClO_4$	25	sol	-1.61	± 0.10	-1.60[d]	± 0.41	[83MAY]
1 M $NaClO_4$	25	sol	-1.62				[83MAY][g]
1 M $NaClO_4$	25	sol	-1.43	± 0.07	-1.42[d]	± 0.69	[91KIM/KLE][n]
1 M $NaClO_4$	30	sol			-1.8	± 0.3	[93LEM/BOY][dk]
1 M $NaClO_4$	50	sol	-2.4	± 0.32	-0.8[dk]	± 0.59	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-0.84	± 1.39	-1.6[dk]	± 0.35	[93LEM/BOY]
1 M NaCl	23	sol	-1.34	± 0.19			[96RUN/NEU][ln]
3 M $NaClO_4$	22	sol	-0.10	± 0.15	-0.01[d]	± 0.17	[86GRE/ROB][f]
3 M $NaClO_4$	25	sol	-0.15	± 0.10	-0.15[d]	± 0.86	[91KIM/KLE][n]
3 M NaCl	23	sol	-0.2	± 0.2			[96RUN/NEU][n]
5 M $NaClO_4$	25	sol	0.41	± 0.10	0.45[d]	± 1.39	[94NEC/KIM][n]
5 M NaCl	25	sol			0.14	± 1.27	[95NEC/RUN][dn]
5 M NaCl	25	sol	0.21				[94NEC/KIM][n]
5 M NaCl	23	sol	0.02	± 0.16			[96RUN/NEU][ln]
$KNpO_2CO_{3(s)}.xH_2O + 2\ CO_3^{-2} \Leftrightarrow K^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O$[x]							
0.2 M K_2CO_3	20±2	sol			-3.3	± 1.5	[66GOR/ZEN][ak]
1 M KCl	75	sol			-2	± 0.63	[93LEM/BOY][dk]
$CsNpO_2CO_{3(s)}.xH_2O + 2\ CO_3^{-2} \Leftrightarrow Cs^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O$[x]							
0.2 M Cs_2CO_3	20±2	sol			-2.7	± 1.5	[66GOR/ZEN][ako]
$NH_4NpO_2CO_{3(s)} + 2\ CO_3^{-2} \Leftrightarrow NH_4^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O$[x]							
0.6 M $(NH_4)_2CO_3$	?	sol			-2.81	± 0.4	[71MOS5][bk]
$Na_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow 3\ Na^+ + NpO_2^+ + 2\ CO_3^{-2} + x\ H_2O$[x]							
0.5 M $NaClO_4$	75	sol			-13.25	± 0.47	[93LEM/BOY][dkh]
1 M $NaClO_4$	30	sol			-13.47	± 0.55	[93LEM/BOY][dhk]
1 M $NaClO_4$	30	sol			-12.97	± 0.62	[93LEM/BOY][dk]
1 M $NaClO_4$	50	sol	-12.90	± 0.22	-14.8[d]	± 0.55	[93LEM/BOY][kh]
1 M $NaClO_4$	75	sol	-14.40	± 1.15	-13.4[d]	± 0.57	[93LEM/BOY][h]

medium	t(°C)	method	$\log_{10}K$		$\log_{10}K$		reference
1 M $NaClO_4$	25	sol	-12.23	± 0.15	-12.25^{d}	± 0.39	[95NEC/RUN]^{n}
3 M $NaClO_4$	25	sol	-12.44		-12.31	± 1.00	[89RIG]^{d}
3 M $NaClO_4$	25	sol			-12.59	± 0.10	[95NEC/RUN]^{dn}
5 M $NaClO_4$	25	sol	-13.57	± 0.11			[95NEC/RUN]^{n}
5 M NaCl	25	sol	-11.46	± 0.23			[95NEC/RUN]^{mn}
5 M NaCl	23	sol	-11.16	± 0.23			[95NEC/FAN]^{ln}
$Na_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow 3\ Na^+ + NpO_2CO_3^- + CO_3^{-2} + x\ H_2O^x$							
0.5 M $NaClO_4$	75	sol			-8.45	± 0.47	[93LEM/BOY]^{dh}
1 M $NaClO_4$	25	sol	-7.73		-7.77^{d}	± 0.30	[95NEC/RUN]^{n}
1 M $NaClO_4$	30	sol	-8.7	± 0.24	-8.2^{dk}	± 0.37	[93LEM/BOY]
1 M $NaClO_4$	50	sol	-7.3	± 0.3	-9.1^{dkh}	± 0.1	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-8.6	± 0.99	-8.2^{dkh}	± 0.2	[93LEM/BOY]
3 M $NaClO_4$	25	sol			-7.06	± 1.00	[89RIG]^{d}
3 M $NaClO_4$	25	sol			-7.83	±0.79	[95NEC/RUN]^{dn}
$K_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow 3\ K^+ + NpO_2CO_3^- + CO_3^{-2} + x\ H_2O^x$							
1 M KCl	75	sol			-9.4	± 0.63	[93LEM/BOY]^{dk}
$Na_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow 3\ Na^+ + NpO_2(CO_3)_2^{3-} + x\ H_2O^x$							
0.5 M $NaClO_4$	75	sol			-6.05	± 0.3	[93LEM/BOY]^{dkh}
1 M $NaClO_4$	30	sol			-6	± 0.1	[93LEM/BOY]^{dkh}
1 M $NaClO_4$	30	sol			-5.5	± 0.41	[93LEM/BOY]^{dk}
1 M $NaClO_4$	50	sol	-6.0	± 0.37	-6^{dkh}	± 0.15	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-5.6	± 1.14	-6.1^{dkh}	± 0.2	[93LEM/BOY]
1 M $NaClO_4$	25	sol	-5.27		-5.3^{d}	± 0.30	[95NEC/RUN]^{n}
3 M $NaClO_4$	25	sol			-4.17^{d}	± 1.00	[89RIG]
3 M $NaClO_4$	25	sol			-4.9^{d}	±0.79	[95NEC/RUN]^{n}
$K_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow 3\ K^+ + NpO_2(CO_3)_2^{3-} + x\ H_2O^x$							
1 M KCl	75	sol			-7.2	± 0.4	[93LEM/BOY]^{dk}
$Na_3NpO_2(CO_3)_{2(s)}.xH_2O + CO_3^{-2} \Leftrightarrow 3\ Na^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O^x$							
0.5 M $NaClO_4$	75	sol			-4.70	± 0.3	[93LEM/BOY]^{dkh}
1 M $NaClO_4$	30	sol			-4.5	± 0.2	[93LEM/BOY]^{dkh}
1 M $NaClO_4$	30	sol			-4	± 0.2	[93LEM/BOY]^{dk}
1 M $NaClO_4$	50	sol	-4.3	± 0.37	-4.5^{dkh}	± 0.3	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-4.3	± 0.83	-4.5^{dkh}	± 0.2	[93LEM/BOY]
1 M $NaClO_4$	25	sol	-3.56	± 0.17	-3.57^{d}	± 0.56	[95NEC/RUN]^{n}
0.5 M Na_2CO_3		sol			-3.72		[77SAI/UEN]^{ak}
0.75 M Na_2CO_3		sol			-2.92		[77SAI/UEN]^{ak}
1 M Na_2CO_3		sol			-2.42		[77SAI/UEN]^{ak}
3 M $NaNO_3$	?	sol			**-1.46**	± 0.09	[77SIM]^{ce}
3 M $NaClO_4$	25	sol	-2.29	± 0.15	-1.67^{d}	± 0.68	[95NEC/RUN]^{n}
3 M $NaClO_4$	22	sol	-1.98		-1.17^{d}	± 0.79	[89RIG]
1.35 M Na_2CO_3		sol			-1.86		[77SAI/UEN]^{ak}
1.6 M Na_2CO_3		sol			-1.42		[77SAI/UEN]^{ak}
5 M $NaClO_4$	25	sol	-2.10	± 0.14			[95NEC/RUN]^{n}
5 M NaCl	25	sol			-1.50	± 0.86	[95NEC/RUN]^{cn}
1.85 M Na_2CO_3		sol			-1.07		[77SAI/UEN]^{ak}
2 M Na_2CO_3		sol			-0.87		[77SAI/UEN]^{ak}
$K_3NpO_2(CO_3)_{2(s)}.xH_2O + CO_3^{-2} \Leftrightarrow 3\ K^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O^x$							
1 M KCl	75	sol			-4.7	± 0.2	[93LEM/BOY]^{dk}
1.2 M K_2CO_3	20	sol			-3.4	± 0.5	[74VIS/VOL]^{ak}
1.2 M K_2CO_3	80	sol			-3.1	± 0.5	[74VIS/VOL]^{ak}
5.57 M K_2CO_3	20±2	sol			-1.4	± 1.5	[66GOR/ZEN]^{ak}
$(NH_4)_3NpO_2(CO_3)_{2(s)}.xH_2O + CO_3^{-2} \Leftrightarrow 3\ NH_4^+ + NpO_2(CO_3)_3^{5-} + x\ H_2O^x$							
2.2 M $(NH_4)_2CO_3$	?	sol			- 2.6	± 0.5	[71MOS5]^{bk}
$Na_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow NaNpO_2CO_{3(s)}.yH_2O + CO_3^{-2} + 2\ Na^+ + (x-y)\ H_2O^x$							
0.5 M $NaClO_4$	75	sol			-3.45	± 0.42	[93LEM/BOY]^{dkh}
1 M $NaClO_4$	30	sol			-2.7	± 0.22	[93LEM/BOY]^{dkh}
1 M $NaClO_4$	30	sol			-2.2	± 0.36	[93LEM/BOY]^{dk}
1 M $NaClO_4$	50	sol	-1.9	± 0.2	-3.7^{dkh}	± 0.51	[93LEM/BOY]
1 M $NaClO_4$	75	sol	-3.46	± 1.12	-2.9^{dkh}	± 0.28	[93LEM/BOY]
1 M $NaClO_4$	25	sol	-2.13		-2.15^{d}	± 0.88	[95NEC/RUN]^{n}

medium	t(°C)	method	$\log_{10}K$		$\log_{10}K$		reference
3 M $NaClO_4$	22	sol	-1.88		-1.66[d]	± 0.15	[89RIG][f]
3 M $NaClO_4$	25	sol	-2.14	± 0.18	-2.12[d]	± 1.10	[95NEC/RUN][n]
5 M $NaClO_4$	25	sol	-2.51	± 0.17	-2.55[d]	± 1.71	[95NEC/RUN][n]
5 M NaCl	25	sol			-1.64[d]	± 1.53	[95NEC/RUN][n]
$K_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow KNpO_2CO_{3(s)}.yH_2O + CO_3^{-2} + 2\ K^+ + (x-y)\ H_2O$[x]							
0.2 to 0.8[j] M K_2CO_3		sol			-0.6	± 0.9	[74SIM/VOL][ak]
1 M KCl	75	sol			-2.7	± 0.6	[93LEM/BOY][dk]
$(NH_4)_3NpO_2(CO_3)_{2(s)}.xH_2O \Leftrightarrow NH_4NpO_2CO_{3(s)}.yH_2O + CO_3^{-2} + 2\ NH_4^+ + (x-y)\ H_2O$[x]							
1.5 to 2.2[j] M $(NH_4)_2CO_3$	?	sol			-0.34	± 0.58	[71MOS5][bk]

[a] Calculated by this review, the data of this publication were not interpreted by the author(s).

[b] Reinterpreted by this review, the author(s) proposed another interpretation of his (their) data; but it was not correct.

[c] Calculated by this review, the author(s) proposed a correct interpretation of this (their) data; but he (they) did not calculate the corresponding equilibrium constant.

[d] Recalculated by this review, following the calculation of the author(s) of the publication.

[e] Value used by this review to select standard value (at I = 0) and eventually $\Delta\varepsilon$ coefficient.

[f] The reference is noted [86GRE/ROB] for a series of Vitorge et al.'s publications that used the same experimental results [84VIT, 85COM, 85KIM, 86GRE/ROB, 89RIG, 91VIT/OLI].

[g] Recalculated in the [93LEM/BOY] publication.

[h] The $Na_3NpO_2(CO_3)_{2(s)}$ solid hydrated phase prepared at room temperature is expected to be partially dehydrated when the temperature is raised above 30°C. This stability constant is for this partially dehydrated high temperature phase.

[i] The same value is reported in the [95NEC/RUN or 94NEC/KIM] report. Some of the uncertainty values are smaller in the [95NEC/RUN] publication, but there were not considered in this table, except at I = 5 M for which no uncertainty was reported in the original report [94NEC/KIM]

[j] In M_2CO_3 aqueous solution, the two M-Np(V)-CO_3 solid phases are at equilibrium for a unique [M_2CO_3] value, $[M_2CO_3]_s$; but since thermodynamic cycles were used the value of the equilibrium constant can be estimated in aqueous solution with M_2CO_3 concentration different from the $[M_2CO_3]_s$ value. This is important only for ionic strength corrections.

[k] Rough estimation.

[l] Data cited in this publication as part of a report by the same laboratory, and that this review did not see.

[m] Corrected by the author for Cl^- complex formation (which is not consistent with the thermodynamic description used by this review).

[n] The references [91KIM/KLE, 94MEI, 94NEC/KIM, 94NEC/RUN, 95FAN/NEC, 95NEC/FAN, 95NEC/RUN, 96FAN/NEC and 96RUN/NEU] report works performed by the same group of authors.

[o] $CsNpO_2CO_{3(s)}$ stoichiometry is not clearly established.

[x] The number of water molecules, x, of the solid phases is not known accurately. It is 3.5 for $NaNpO_2CO_{3(s)}$ at equilibrium under 30°C; but it could be less for freshly precipitated compounds. Theoretical ionic strength correction on solubility products (including a x $\log_{10}a_{H_2O}$ term) is then not known accurately.

No evidence of the following species

The values of the formation constants, K, proposed by the authors are not consistent with other published works (tabulated above)

medium	equilibrium	t(°C)	method	$\log_{10}K$	reference
?	$NpO_2^{2} + HCO_3^- \Leftrightarrow NpO_2HCO_{3(aq)}$?		?	-2.2	[63MOS/GEL]
0		?	?	-2.4	
$(NH_4)_2CO_3$	$NpO_2^+ + H_2O + CO_3^{2-} \Leftrightarrow NpO_2OHCO_3^{-2} + H^+$?		sol	-9.18 ± 0.12	[71MOS5]
$(NH_4)_2CO_3$	$NpO_2^+ + H_2O + 2\ CO_3^{2-} \Leftrightarrow NpO_2OH(CO_3)_2^{-4} + H^+$?			-9.26 ± 0.05	[71MOS5]

Appendix A

[54NIG/PEN]

Nigon, J.P., Penneman, R.A., Staritzky, E., Keenan, T.K., Aspery, Z.B. *Alkali carbonates of Np(V), Pu(V) and Am(V)*, J. Phys. Chem., 58, 5 (1954) 403-404.

This paper reports the preparation of $MAnO_2CO_{3(s)}$ hydrated compounds for $M^+ = Na^+$, K^+, Rb^+ or NH_4^+, and $AnO_2^+ = NpO_2^+$, PuO_2^+ and AmO_2^+. This is the first published paper concerning Np(V) carbonate chemistry. Nigon et al. precipitated Np(V) in a 0.1 M K_2CO_3 solution. The solid phase was assumed to be $KAnO_2CO_{3(s)}$; but several hydrated phases might exist in these conditions. Anyhow, no data from this work could be used by the present review.

[63MOS/GEL]

Moskvin, A.I., Geletseanu, I., Lapitskii, A.V. *Certain regularities of complex formation by pentavalent actinide elements*, Doklady Chem., 149, 1-6 (Mar-Apr 1963) 264-266.

Moskvin, Geletseanu and Lapitskii report from "unpublished" work, the values $\log_{10}K = -2.2$ at I = 0.15 M and -2.4 at 0 M, for the $NpO_2HCO_{3(aq)}$ formation constant. There is no indication about the ionic strength correction, the experimental procedure, the interpretation (of the experimental results), nor the definition of the stability constant. OH^-, HCO_3^- and CO_3^{-2} anions are in competition to form Np(V) complexes, and high CO_2 partial pressure conditions are more likely to stabilise this $NpO_2HCO_{3(aq)}$ species; but no evidence of any Np(V) bicarbonate complex was found by this review even from later works, that used saturated CO_2 conditions [84VIT 86GRE/ROB, 89RIG]. The data proposed in that publication are then in error. Later work by one of the authors [71MOS5] proposed the formation of other Np(V) soluble complexes.

[64KEE/KRU]

Keenan, T.K., Kruse, F.H. *Potassium double carbonates of pentavalent neptunium, plutonium and americium*, Inorg. Chem., 3 (1964) 1231-1232.

Keenan and Kruse prepared $KNpO_2CO_{3(s)}$, $KPuO_2CO_{3(s)}$ and $KAmO_2CO_{3(s)}$ hydrated compounds, by precipitation in 0.1 M $KHCO_3$ solution. X-ray powder diffraction patterns were observed and calculated; but several hydrated phases can possibly be prepared in similar conditions. Anyhow no data from this work was used by the present review.

[65KEE]

Keenan T. K., *Lattice Constants of Some Alkali Metal Actinyl(V) Compounds*. Inorg. Chem. 4, 10 (1965) 1500-1501.

Keenan claimed that he prepared a $CsAmO_2CO_{3(s)}$ compound. He characterised it by its X-ray diffraction pattern and proposed the same structure as for the $KNpO_2CO_{3(s)}$, $KPuO_2CO_{3(s)}$ and $KAmO_2CO_{3(s)}$ hydrated compounds, that he prepared previously [64KEE/KRU]; but he found that one of the lattice parameter of his $CsAmO_2CO_{3(s)}$ compound was quite different from the corresponding one of the other compounds. He did not comment this. He also did not report the preparation of the $CsNpO_2CO_{3(s)}$ compound (Np(V) is more stable than Am(V)). So this review did not consider that the formation of this $CsNpO_2CO_{3(s)}$ compound was established. Still, $CsNpO_2CO_{3(s)}$ more or less hydrated compounds with lattice parameters different from corresponding sodium hydrated compounds might well be stable, because Cs^+ is usually less hydrated than Na^+: it has been proposed that the variation in the lattice parameters was correlated with hydration or with the exchange between Np(V) and Na(2 H_2O). This review considered that this type of explanation was reasonable; but not well established.

[66GOR/ZEN]

Gorbenko-Germanov, D.S., Zenkova, R.A. *Potassium and caesium dioxotricarbonatoneptunates(V)*, Russ. J. Inorg. Chem., 11(3) (1966) 282-287.

Gorbenko-Germanov and Zenkova prepared M-Np(V)-CO_3 solid compounds, for M = K or Cs. From chemical analysis, they claimed that these compounds were $M_5NpO_2(CO_3)_{3(s)}$; but such solid phases were never confirmed in any later publications, and the solubility measurements reported in this [66GOR/ZEN] work showed, that equilibrium was probably not obtained for the preparation of the initial solid phase (as explained below). It was also claimed later [74VIS/VOL] that hydrated $K_3NpO_2(CO_3)_{2(s)}$ and not $K_5NpO_2(CO_3)_{3(s)}$ was formed in similar conditions.

The authors measured Np(V) concentration in the "mother-liquor" (50 % M_2CO_3 aqueous solution) and in 0.2 M M_2CO_3 aqueous "wash solution". They then equilibrated each "$M_5NpO_2(CO_3)_{3(s)}$" solid phase during one week at 20 ± 2°C in these two M_2CO_3 aqueous solutions, and in water, to measure Np(V) solubility. The Np(V) solubility (after one week then) was always less than the total Np(V) concentration determined in the corresponding initial "mother-liquor" or "wash solution". This was an evidence of slow transformation of the initial M-Np(V)-CO_3 solid compound into another more stable one. This review tried to interpret the [66GOR/ZEN] solubility measurements with the:

$$MNpO_2CO_{3(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-} + M^+$$

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

equilibria; but there is no way to check whether equilibrium was obtained before the solubility measurements. There is only one experimental result (Np(V) solubility in 0.2 M M_2CO_3) that could be used to estimate equilibrium constant, but in this condition the Np(V) aqueous speciation is not known (namely the $[NpO_2(CO_3)_3^{5-}]$ / $[NpO_2(CO_3)_2^{3-}]$ ratio), because the activity coefficients are not known and have different values in Na^+ and K^+ media: typically in 0.2 M Na_2CO_3 aqueous solution the $[NpO_2(CO_3)_3^{5-}]$ / $[NpO_2(CO_3)_2^{3-}]$ is about 1. This review still estimated the equilibrium constant $K_{s1,3}$, and increased the uncertainties to account for the above assumptions:

$\log_{10}K_{s1,3}$ = -3.3 ± 1.5 in 0.2 M K_2CO_3 aqueous solution at 20 ± 2°C

in the same way;

$\log_{10}K_{s1,3}$ = -2.7 ± 1.5 in 0.2 M Cs_2CO_3 aqueous solution at 20 ± 2°C could also be estimated; but the $CsAnO_2CO_{3(s)}$ formation is questionable (see the discussion on the [65KEE] publication in this appendix).

This review assumed that the solubility measured in the most concentrated K_2CO_3 aqueous solutions was controlled by the

$$K_3NpO_2(CO_3)_{2(s)}, + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ K^+$$

equilibrium, and calculated:

$\log_{10}K_{s2,3}$ = -1.4 ± 1.5 in 5.57 M K_2CO_3 aqueous solution at 20 ± 2°C

The uncertainty has been increased by this review because equilibrium was probably not obtained prior to solubility the measurements.

The same type of interpretation might be less valid for the 50 % Cs_2CO_3 media, where the Np(V) solubility is quite higher than in the sodium or potassium aqueous solutions. There are indications on the $Rb_3NpO_2(CO_3)_{2(s)}$ solid phase in the literature [79VOL/VIS2, 81VOL/VIS, 81VOL/VIS2, 81VOL/VIS4]; but not about the $Cs_3NpO_2(CO_3)_{2(s)}$ one. It is then not clear whether the $Cs_3NpO_2(CO_3)_{2(s)}$ solid was formed. This review does not then propose further interpretation of the solubility measurements in concentrated Cs_2CO_3 aqueous solution. Finally a reasonable interpretation of this work could be proposed, and it is consistent with the Np(V) behaviour in carbonate media as proposed by this review. Still, the thermodynamic data extracted from this publication by this review are only rough estimations and the corresponding solid phases were not actually characterised.

Two Np(V) absorption spectra were also reported. The characteristic NpO_2^+ bands were notably changed when adding concentrated carbonate solution. This is then the first evidence of the formation of soluble Np(V) complex. The spectra can be attributed to a mixture of $NpO_2(CO_3)_3^{5-}$ and $NpO_2(CO_3)_2^{3-}$ complexes [89RIG]; but there are not enough results to estimate a formation constant.

[71MOS5]

Moskvin, A.I. *Complex formation of neptunium(IV, V, VI) in carbonate solutions*. Radiokhimiya, 13(5) (1971) 674-681, in Russian; Engl. transl.: Sov. Radiochem., 13 (5) (1971) 694-699.

In this publication Moskvin proposed the stoichiometry of Np(V) soluble carbonate complexes, and their stability constants. This interpretation was not proven, it was in contradiction with later work; but the experimental observations presented in this work are consistent with the Np(V) behaviour in concentrated carbonate media deduced from later works. Unfortunately Moskvin's erroneous interpretation was widely and repetitively cited. Moskvin reported Np(V) solubility measurements in $(NH_4)_2CO_3$ concentrated solutions, using either $NpO_2OH_{(s)}$ or hydrated $NH_4NpO_2CO_{3(s)}$ solids as starting materials. He did not report any characterisation of the solid phase. The author did not notice that the initial solid phase has little influence on most of his solubility results: this is an indication, that at least one of the initial solid phases were transformed during the solubility equilibration. Moskvin did not give any indication on pH calibration (junction potential, ionic strength effects). In contradiction with his previous publication [63MOS/GEL], Moskvin assumed that the $NpO_2OHCO_3^{2-}$ and $NpO_2OH(CO_3)_2^{4-}$ complexes were formed. The author did not try any other model (i.e. other set of soluble complexes and solid phases). He assumed, that the initial solid phase did not change during the equilibration, and that the free carbonate concentration, $[CO_3^{2-}]$, was equal to the total carbonate concentration, which is wrong because his measured pH were always less than the pK_a value for the HCO_3^{2-}/CO_3^{2-} couple. $(NH_4)_2CO_{3(s)}$ dissolution buffers the pH according to the following equilibrium

$$NH_4^+ + CO_3^{2-} \Leftrightarrow NH_3 + HCO_3^-$$

Moskvin's interpretation is then not reliable; but his Np(V) solubility measurements are quite consistent with previous [66GOR/ZEN] and later [77SIM 84VIT 86GRE/ROB 91KIM/KLE 94NEC/KIM] works in similar media. When $(NH_4)_2CO_3$ was added to the solution, this review assumed that the $NpO_2OH_{(s)}$ solid was transformed into a hydrated $NH_4NpO_2CO_{3(s)}$ one, which was slowly transformed into a thermodynamically more stable (hence less soluble) hydrated $(NH_4)_3NpO_2(CO_3)_{2(s)}$ solid in the most concentrated $(NH_4)_2CO_3$ aqueous solutions (2 and 2.2 M). This review reinterpreted Moskvin's data, disregarding his pH measurements (pH values calculated by this review in $(NH_4)_2CO_3$ buffers were used instead) and using k_3 and $K_{s1,3}$, the constants of the following equilibria respectively:

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

$$NH_4NpO_2CO_{3(s)} + 2\ CO_3^{2-} \Leftrightarrow NH_4^+ + NpO_2(CO_3)_3^{5-}$$

The data in 2 and 2.2 M $(NH_4)_2CO_3$ were not taken into account, to estimate the corresponding equilibrium constants, since a hydrated $(NH_4)_3NpO_2(CO_3)_{2(s)}$ solid phase was probably (slowly) precipitating in these conditions. The $NpO_2OH_{(s)}$ solubility data were also excluded, since the equilibration achievement was certainly poorer: $NpO_2OH_{(s)}$ solubility results were more scattered and higher than the $NH_4NpO_2CO_{3(s)}$ ones. The Np(V) standard complexation constants and the specific interaction coefficients selected or estimated by this review were used; but the uncertainty has been increased for the following analogies:

$\varepsilon(K^+,CO_3^{2-}) \approx \varepsilon(NH_4^+,CO_3^{2-}) = 0.02 \pm 0.1$
and $\varepsilon(Na^+,HCO_3^-) \approx \varepsilon(NH_4^+,HCO_3^-) = 0 \pm 0.2$.

$\varepsilon(NpO_2(CO_3)_3^{5-},NH_4^+)$, $\varepsilon(NpO_2(CO_3)_2^{3-},NH_4^+)$ and $Ks_{1,3} = Ks_1\ \beta_3 = [NH_4^+]\ [NpO_2(CO_3)_3^{5-}]\ /\ [CO_3^{2-}]^2$ were fitted by this review from Moskvin's data, while the $\log_{10}k_3 = -0.87$ value was fixed because fitted values of the $\varepsilon(NpO_2(CO_3)_2^{3-},NH_4^+)$ and k_2 parameters were correlated (it was then not much consistent to fit them together):

$\log_{10}Ks_{1,3}° = -6.27 \pm 0.34$, value was found
$\varepsilon(NpO_2(CO_3)_2^{3-},NH_4^+) = -0.17 \pm 0.20$
$\varepsilon(NpO_2(CO_3)_3^{5-},NH_4^+) = 0.6$ where used;
only $\varepsilon(NpO_2(CO_3)_3^{5-},NH_4^+) \geq 0.4$ could be determined

These numerical values do not seem reasonable: it is not clear whether this is due to an actual ion pair interaction effect between the NH_4^+ cation and the highly negatively charged $NpO_2(CO_3)_3^{5-}$ ion, or to the poor quality of the experimental solubility measurements (the solid phase was not characterised, and the [71MOS5] publication does not contain the information necessary to verify whether true equilibrium was obtained). The log(solubility) vs. log[CO_3^{-2}] curve is expected to be a straight line with slope 2 when the solubility is mainly due to the limiting complex, and when neglecting ionic strength correction. In the above calculation, the effect of the $\varepsilon(NpO_2(CO_3)_3^{5-},NH_4^+)$ fitted parameter was to change the slope from this ideal value of 2, to the experimental observation which is about 1. 1 is also the ideal value when the limiting complex is dissociated into the $NpO_2(CO_3)_2^{3-}$ one which is then consistent with the above numerical result (indicating the limiting complex was not predominating). On the other hand ionic strength correction is expected, and solid phase transformation would have the same effect. The $\varepsilon(NpO_2(CO_3)_3^{5-},NH_4^+)$ value could not be correctly fitted: the experimental data do not allow to check whether the SIT is still valid, specially whether $\varepsilon(NpO_2(CO_3)_3^{5-},NH_4^+)$ is constant in 0.1 to 1.8 M $(NH_4)_2CO_3$ aqueous solutions. This was taken into account for the uncertainty estimation on the other fitted parameters. Due to ionic strength effects, the fitting results indicate, that the $NpO_2(CO_3)_2^{3-}$ complex, and not the limiting one, $NpO_2(CO_3)_3^{5-}$, would have been predominating in Moskvin's study: this is quite surprising. In this publication absorption spectra were also reported in concentrated $(NH_4)_2CO_3$ aqueous solutions of Np(IV) and Np(VI), but not for Np(V). It is then not possible to check, which complex was formed (from other [66GOR/ZEN, 75UEN/SAI, 89RIG] published spectra). Still the $NpO_2(CO_3)_3^{5-}$ molar absorptivity is very low: it is quite difficult to detect its spectrum in the 0.12 mM Np(V) solutions used by Moskvin, who possibly did not report it for this reason. This review also tested another interpretation of these solubility data by assuming that the limiting complex was predominating (this is then in contradiction with the previous interpretation). A classical SIT regression in 0.2 to 1.8 M $(NH_4)_2CO_3$ aqueous solution assuming that only the limiting complex, $NpO_2(CO_3)^{5-}$, was predominating gave:

$\log_{10}Ks_{1,3}^\circ = -6.01 \pm 0.40$
and $\Delta\varepsilon = 0.64 \pm 0.27$
hence $\varepsilon(NpO_2(CO_3)^{5-},NH_4^+) = 0.60 \pm 0.5$

Both interpretations lead to the same $Ks_{1,3}$ and $\varepsilon(NpO_2(CO_3)^{5-},NH_4^+)$ values, while they rely on contradictory assumptions. There is then no consistent interpretation of Moskvin's data. This difficulty is certainly due to the poor achievement of Moskvin's solubility equilibration. This review did not select a value extrapolated to zero ionic strength; and calculated the following values assuming that the limiting complex was formed. The uncertainty estimation took into account the above discussion on possible systematic error in the Np(V) aqueous speciation, and on solid phase transformation. The solid phase was not characterised by the author so this review only propose the value in 0.6 M $(NH_4)_2CO_3$ (that is not far from the sodium system one as calculated from the data selected by this review), since there is an alternative possible and reasonable interpretation at higher ionic strength.

$[(NH_4)_2CO_3]$	0.2	0.6	1	1.25	1.5
$\log_{10}K_{s1,3}$	-2.70 ± 1.0	-2.81 ± 0.4	-2.99 ± 0.3	-2.92 ± 0.2	-2.94 ± 0.3

These $K_{s1,3}$ values for a $NH_4NpO_2CO_{3(s)}$ hydrated solid, are quite different from the potassium one estimated by this review (see the discussion on the [66GOR/ZEN] publication in this appendix); while K^+ and NH_4^+ cation have often similar chemical behaviour. The ionic strength influence in $(NH_4)_2CO_3$ aqueous solutions, on the above $K_{s1,3}$ values, is different from the corresponding compound in sodium media (as observed by this review from the [75UEN/SAI, 83MAY, 86GRE/ROB, 91KIM/KLE, 94NEC/KIM] publications). No conclusion can be proposed to explain such differences, since the $K_{s1,3}$ values in ammonium and potassium media are only rough estimation where solid phase was not characterised. Another alternative explanation is that for most of these experimental data, equilibrium was not obtained (solid phase was typically transforming to the hydrated $(NH_4)_3NpO_2(CO_3)_{2(s)}$) or was controlled by another intermediary solid phase.

From the measurements in 2.2 M $(NH_4)_2CO_3$ aqueous solutions this review estimated the constant for the following equilibrium, it is only a guide line value since the solid phase was not characterised by the author:

$$(NH_4)_3NpO_2(CO_3)_{2(s)} + 2\ CO_3^{2-} \Leftrightarrow 3\ NH_4^+ + NpO_2(CO_3)_3^{5-}$$

$\log_{10}Ks_{2,3} = -2.6 \pm 0.5$ in 2.2 M $(NH_4)_2CO_3$ aqueous solution.

This $Ks_{2,3}$ value is similar to the corresponding one in potassium media as estimated by this review (see the discussion on the [66GOR/ZEN] publication in this appendix). From the above values, this review estimated the constant

$\log_{10}Ks_{2,3}/Ks_{1,3} = -0.34 \pm 0.58$ in 2.2 M $(NH_4)_2CO_3$ aqueous solution.

for the following equilibrium $(NH_4)_3NpO_2(CO_3)_{2(s)} \Leftrightarrow NH_4NpO_2CO_{3(s)} + CO_3^{-2} + 2\ NH_4^+$

[73KHA/MOS]

Kharitonov Y.Y., Moskvin, A.I. *IR absorption spectra of some neptunium compounds. III. carbonate compounds*. Radiokhimiya, 15 (2) (1973) 246-249, in Russian; Engl. transl.: Sov. Radiochem., 15 (2) (1973) 240-243.

Kharitonov and Moskvin interpreted infrared spectroscopy spectra with mono and bidentate bounds between NpO_2^+ and CO_3^{2-} in a $NH_4NpO_2CO_{3(s)}$ solid compound.

[74SIM/VOL]

Simakin G.A., Volkov Yu.F., Visyashcheva G.I., Kapsukov I.I., Baklanova P.F., Yakovlev G.N. Carbonate compounds of pentavalent actinides with alkali metal cations. II. *Preparation of carbonate compounds of Np(V), Pu(V) and Am(V) from K_2CO_3 solution by electrochemical reduction*. Radiokhimiya, 16 (6) (1974) 859-863, in Russian; Engl. transl.: Sov. Radiochem., 16 (6) (1974) 838-841.

The author prepared $KNpO_2CO_{3(s)}$ and $K_3NpO_2(CO_3)_{2(s)}$ hydrated compounds in respectively 0.2 and 0.8 M K_2CO_3 aqueous solution. These preparation conditions were respectively less and more than the [CO_3^{-2}] value controlled by the

$$KNpO_2CO_{3(s)} + CO_3^{-2} + 2\ K^+ \Leftrightarrow K_3NpO_2(CO_3)_{2(s)}$$

equilibrium. This review then estimated the constant, K, of this equilibrium

$\log_{10}K = \log_{10}K_{s2} - \log_{10}K_{s1} = -0.6 \pm 0.9$

[74VIS/VOL]

Visyashcheva, G.I., Volkov, Y.F., Simakin, G.A., Kapshukov, I.I., Bevz, A.S., Yakovlev, G.N. *Carbonate compounds of pentavalent actinides with alkali metal cations: I. Composition and some properties of solid carbonates of pentavalent neptunium with potassium obtained from K_2CO_3 solutions*, Sov. Radiochem., 16 (1974) 832-837. Translated from Radiokhim., 16 (1974) 853-859.

Visyashcheva, Volkov, Simakin et al. prepared $KNpO_2CO_{3(s)}$ and $K_3NpO_2(CO_3)_{2(s)}$ hydrated solid phases that they characterised by chemical analysis and X-ray diffraction. Hydrated $KNpO_2CO_{3(s)}$ was precipitated in concentrated 0.1 - 0.2 M K_2CO_3 aqueous solutions. The ratio Np(V)/CO_3^{2-} in the solid was titrated. The Np oxidation state was controlled. Np(V) potentiometric (pH) titration using 0.2 M K_2CO_3 solution confirmed the stoichiometry of the hydrated $KNpO_2CO_{3(s)}$ solid. This technique was also used to confirm the stoichiometry $K_3NpO_2(CO_3)_{2(s)}$. From the X-ray powder diffraction patterns it was deduced that two $K_3NpO_2(CO_3)_{2(s)}$ hydrated phases were formed. One precipitated from 0.8-1.5 M K_2CO_3 solutions, and the other one from 1.8-5.6 M K_2CO_3 solutions. They assumed that there were other solid phases (with the same stoichiometry or $K_5NpO_2(CO_3)_{3(s)}$); but this review considered that this conclusion was not actually supported by the X-ray diffraction patterns given in this work. It is quite surprising that two different solid phases with the same stoichiometry could be in equilibrium in aqueous solution: it is (thermodynamically) possible only when the two solid phases are two different hydrated compounds, observation of the two different phases could then only be due to the variation of the water activity. This is quite unusual since the variations of the water activity are relatively small. The precipitation of the two different solid phases could also be due to kinetics.

Potentiometric titration of a 0.06 M Np(V) aqueous solution with a 0.2 M K_2CO_3 aqueous solution showed that the precipitation started at pH = 4.6, and that the pH was buffered up to pH = 5.6 (before the equivalent point), the half point reaction was at pH = 5.2. Back titration of the solid compounds, with 0.1 M HCl, showed buffering of the pH at about the same values, the half point reaction was at pH = 4.8, 5.2 and 6.4 respectively for hydrated $K_3NpO_2(CO_3)_{2(s)}$, hydrated $KNpO_2CO_{3(s)}$ and a K_2CO_3 solution. In these conditions, the free carbonate concentration, $[CO_3^{-2}]$, was certainly less than 10 µM so NpO_2^+ was not complexed, and according to the data selected by this review, the titration reactions were then

$$K^+ + NpO_2^+ + CO_2 + H_2O \Leftrightarrow KNpO_2CO_{3(s)} + 2\,H^+$$

$$KNpO_2CO_{3(s)} + 2\,H^+ \Leftrightarrow K^+ + NpO_2^+ + CO_2 + H_2O$$

$$K_3NpO_2(CO_3)_{2(s)} + 4\,H^+ \Leftrightarrow 3\,K^+ + NpO_2^+ + 2\,CO_2 + 2\,H_2O$$

Assuming that titration was inducing $CO_{2(g)}$ bubbling (hence $P_{CO2} \approx 1$ atm), and that the NpO_2^+ concentration at the half point reactions was about 0.03 M. This review estimated the solubility products

$$K_{s1} \approx -10.3 \pm 2.0$$

but this value is not much reliable, because P_{CO2} and $[NpO_2^+]$ had to be estimated (they were not measured or reported in this publication [74VIS/VOL]). Anyhow, the potentiometric titration results are not much consistent with a later work in sodium (instead of potassium) media by the same group of authors [79VOL/VIS], and this can be attributed to kinetics (see the discussion of the publication [79VOL/VIS] in this appendix).

The authors also reported Np(V) solubility values in 1.2 M K_2CO_3 aqueous solutions at 20 and 80°C. This review assumed that this solubility was controlled by the following equilibrium

$$K_3NpO_2(CO_3)_{2(s)} + CO_3^{-2} \Leftrightarrow 3\,K^+ + NpO_2(CO_3)_3^{-5}$$

and then calculated

$\log_{10}K_{s2,3} \approx -3.4 \pm 0.5$ in 1.2 M K_2CO_3 aqueous solutions at 20°C,

and $\log_{10}K_{s2,3} \approx -3.1 \pm 0.5$ in 1.2 M K_2CO_3 aqueous solutions at 80°C.

These values are consistent with a previous estimation (see the discussion of the [66GOR/ZEN] publication in this appendix) within the uncertainties (that was also increased for this comparison since the ionic strength were not the same in the two measurements). The new value [74VIS/VOL] is more accurate since the solid phase was prepared more carefully here; but it was not possible to verify whether the solid phase did not change between 20 and 80°C.

[74VOL/KAP]

Volkov, Y.F., Kapshukov, I.I., Visyashcheva, G.I., Yakovlev, G.N. *Carbonate compounds of pentavalent actinides with alkali metals cations: III. x-ray investigation of Np(V), Pu(V) and Am(V) monocarbonates with potassium*, Sov. Radiochem., 16, 6 (1974) 842-845. Transl. from Radiokhim., 16, 6 (1974)863-867.

Volkov, Kapshukov, Visyashcheva and Yakovlev prepared $KAnO_2CO_{3(s)}$ hydrated compounds, where An was Np, Pu or Am. They discussed the variations observed in their X-ray diffraction patterns as a function of preparation conditions and ageing. This interpretation seems reasonable (variation of the distance between some crystal lattices); but the most important information for the selection of thermodynamic data, is that it is difficult to obtain a well-characterised solid phase of this type, in equilibrium with aqueous solution.

[74VOL/KAP2]

Volkov, Y.F., Kapshukov, I.I., Visyashcheva, G.I., Yakovlev, G.N. *Carbonate compounds of pentavalent actinides with alkali metals cations: IV. x-ray investigation of dicarbonates of Np(V), Pu(V) and Am(V) with potassium*, Sov. Radiochem., 16, 6 (1974) 846-850. Transl. from Radiokhim., 16, 6 (1974) 868-873.

In this publication, Volkov, Kapshukov, Visyashcheva and Yakovlev reported the X-ray diffraction patterns of a hydrated $K_3AnO_2(CO_3)_{2(s)}$ solid compounds, where An = Np, Pu or Am. They discussed the temperature influence on the lattice parameters. No thermodynamic data can be extracted from this work.

[75UEN/SAI]

Ueno, K., Saito, A. *Solubility and absorption spectra of a carbonato complex of pentavalent neptunium*, Radiochem. Radioanal. Letters, 22(2) (1975) 127-133.

Ueno and Saito have measured the Np(V) solubility in 0.05 to 1.6 M Na_2CO_3 solutions. The ionic strength was then varying. In the most concentrated Na_2CO_3 solutions, the solid was probably slowly transformed into a hydrated $Na_3NpO_2(CO_3)_{2(s)}$ one [81VOL/VIS3, 66GOR/ZEN, 86GRE/ROB, 93LEM/BOY and 95NEC/RUN]. Np(V) absorption spectra in 0.5 to 2 M Na_2CO_3 solutions reported in this work, are similar to those obtained in other works [66GOR/ZEN, 89RIG]. The authors did not interpret their results; but they appeared to be consistent with the Np(V) solubility predicted by using the data selected by this review (from other published works). To calculate the Np(V) solubility in Na_2CO_3 solutions, this review calculated the carbonate speciation assuming equilibrium with the air, used the following equilibria

$$NaNpO_2CO_{3(s)} \Leftrightarrow NpO_2CO_3^- + Na^+$$

$$NpO_2CO_3^- + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$$

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

and the corresponding values of the equilibrium constants and SIT coefficients calculated from those selected by this review. This calculated solubility is in very good agreement with Ueno and Saito's solubility measurements in 0.05 to 0.6 M Na_2CO_3 solutions; but for curve fitting, too many parameters were involved for the number of experimental data: there are 8 solubility measurements, for 6 significant parameters (the above 3 equilibrium constants, and 3 SIT coefficients) to be fitted. This review then only fitted K_{s1}, the solubility product of a hydrated $NaNpO_2CO_{3(s)}$.

$\log_{10}K_{s1} = -11.22 \pm 0.35$ at $I = 0$

This K_{s1} fitted value is in fair agreement with the ones selected by this review. this review still did not use the results of this [75UEN/SAI] publication to proposes a selected value, since too may parameters were not controlled in that work. The

$$NaNpO_2CO_{3(s)} + 2\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + Na^+$$

equilibrium was controlling the Np(V) solubility for the experimental data which were used by this review to fit the above K_{s1} value, the corresponding $K_{s1,3}$, stability constant was then deduced by this review from Ueno and Saito measurements

$[Na_2CO_3]$ (mol.l^{-1})	0	0.4	0.3	0.2	0.15	0.1	0.07
$\log_{10}K_{s1,3}$	-5.66 ± 0.21	-1.72 ± 0.39	-1.78 ± 0.42	-1.97 ± 0.51	-2.58 ± 0.64	-2.92 ± 0.92	-3.04 ± 1.25

These values are again in fair agreement with the later experimental data selected by this review to propose equilibrium constant. This comparison indicates that these $K_{s1,3}$ values deduced from Ueno and Saito measurements correspond to a freshly precipitated compound, since they were a little bigger than those proposed in the [83MAY and 86GRE/ROB] publications.

In the 1.2 and 1.6 M Na_2CO_3 solutions, the measured solubility was below the above calculated solubility: this is an evidence of the precipitation of a new solid phase, which was certainly $Na_3NpO_2(CO_3)_{2(s)}$, [77SIM, 79VOL/VIS2, 81VOL/VIS, 81VOL/VIS2, 81VOL/VIS4]. This solubility should then be interpreted with the following equilibrium

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ Na^+$$

for which this review estimated

$\log_{10}Ks_{2,3} < -0.43$ in 1.6 M Na_2CO_3 solution.

Still, there is no way to check the equilibrium achievement in that work: for this reason, this review only proposed a maximum value.

[76VOL/VIS]

Volkov, Y.F., Visyashcheva, G.I., Kapshukov, I.I., Simakin, G.A., Yakovlev, G.N. *Composition and properties of carbonates of the pentavalent actinides.* Sov. Radiochem., 18, 1 (1976) 88-92. Transl. from Radiokhim., 18, 1 (1976) 96-100.

In this publication, Volkov, Visyashcheva, Kapshukov, Simakin, and Yakovlev discussed their previous results [74VOL/KAP, 74VOL/KAP2]. No thermodynamic data could be extracted from this publication.

[77SAI/UEN]

Saito A., Ueno, K. *The precipitation of some actinide element complex ions by using hexammine cobalt(III) cation, V.: Absorption spectra and the precipitation of Np(IV), (V) and (VI) carbonate complex ions*. J. Inorg. Nucl. Chem., 39 (1977) 315-318.

Saito and Ueno introduced Np(V) in concentrated Na_2CO_3 and $Co(NH_3)_6Cl_3$ aqueous solutions. From chemical analysis, they assumed that the $(Co(NH_3)_6)_8(NpO_2)_6(CO_3)_{15(s)}$ solid compound were formed. According to this interpretation, this review deduced that the solubility should be controled by the the following equilibrium

$$(Co(NH_3)_6)_{4/3}NpO_2(CO_3)_{5/2(s)} + 0.5\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_3^{-5} + 4/3\ Co(NH_3)_6^{+3}$$

which is different from the expected equilibrium when no $Co(NH_3)_6Cl_3$ is added:

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_3^{-5} + 3\ Na^+$$

The corresponding solubility was calculated by using the data selected by this review (including activity coefficient corrections on the shape of this curve). The figure 4 of the [77SAI/UEN] publication was scanned, and the $\log_{10}[Np(V)]$ data at constant (0.04 M) $Co(NH_3)_6Cl_3$ concentration, were plotted as a function of $\log_{10}[Na_2CO_3]$. The curve calculated for $Na_3NpO_2(CO_3)_{2(s)}$ solubility, is below Saito and Ueno's solubility results by (only) less than 0.3 unit $\log_{10}$, and this curve is parallel to these [77SAI/UEN] points. This is not much consistent, since the stoichiometric coefficients of the above two solubility equilibria are completely different. On the other hand, this slope analysis is dependent on the activity coefficients, that varied dramatically in this particular case; but the $\varepsilon(Co(NH_3)_6^{+3}, CO_3^{-2})$ value is not known and its contribution cannot be estimated. So no conclusion can be proposed for the validity of Saito and Ueno's interpretation, and this review did not consider the $(Co(NH_3)_6)_8(NpO_2)_6(CO_3)_{15(s)}$ solid compound. In 0.04 M $Co(NH_3)_6Cl_3$ this review calculated the following values for the constant of the last above equilibrium, assuming $[CO_3^{-2}] = [Na_2CO_3]$. The value at zero ionic strength was calculated using the other needed values selected by this review (equilibrium constants for the other equililbria and the ionic strength corrections).

$[Na_2CO_3]$	0	0.5	0.75	1	1.35	1.6	1.85	2
$\log_{10}K_{s2,3}$	-9.45	-3.72	-2.92	-2.42	-1.86	-1.42	-1.07	-0.87

[77SIM]

Simakin G.A. *Real oxidation potentials of the couples AmO_2^{2+}-AmO_2^{+}, NpO_2^{2+}-NpO_2^{+} in solutions of potassium and sodium carbonates*. Radiokhimiya, 19 (4) (1977) 518-521 Engl. transl.: Sov. Radiochem., 19 (4) (1977) 424-426.

This publication reports very useful piece of experimental works on Np(V) and Np(VI) chemistry in concentrated carbonate media. It is the first publication in which the stoichiometry of a soluble Np(V) carbonate complex is reasonably well established (it is the limiting complex). It is also the first publication that produced reliable measurements of the Np(VI)/Np(V) redox couple in carbonate media from which the stoichiometry of the Np(VI) carbonate limiting complex was correctly deduced.

...Simakin's interpretation assumed that the solubility was controled by the

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ Na^+$$

equilibrium. This review scanned the experimental solubility data from the figure 2 of this publication and followed Simakin's interpretation to determine then

$\log_{10}Ks_{2,3} = -1.46 \pm 0.09$, at I = 3M ($NaNO_3$)

This review also tried to estimate k_3, the constant of the following equilibrium

$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$

from Simakin's solubility measurement. For this, k_3 and $Ks_{2,3}$ were fitted together, and the following results were found:

$\log_{10}Ks_{2,3} = -1.47 \pm 0.08$ at I = 3M ($NaNO_3$)
and $\log_{10}k_3 = 1.79$ at I = 3M ($NaNO_3$);

but this determination of k_3 is not much reliable since $NpO_2(CO_3)_2^{3-}$ contribution to the solubility was always less than 7 % which is less than the experimental accuracy. So this review fixed the k_3 value do the one calculated from the data selected by this review

$\log_{10}k_3 = 2.51$ at I = 3M ($NaNO_3$); which is in fair agreement with
$\log_{10}k_3 = 2.49 \pm 0.07$ at I = 3M ($NaClO_4$)

as recalculated by this review from the data reported in the [86GRE/ROB] publication. The result is practically the same:

$\log_{10}Ks_{2,3} = -1.46 \pm 0.09$ at I = 3M ($NaNO_3$)

[77VOL/VIS]

Volkov, Yu.F., Visyashcheva, G.I., Kapshukov, I.I. *Study of carbonate compounds of pentavalent actinides with alkali metal cations: V. Production and identification of hydrate forms of sodium monocarbonatoneptunaylate*, Sov. Radiochem., 19, 3 (1977) 263-266. Transl. Radiokhim., 19, 3 (1977) 319-323.

Volkov, Visyashcheva and Kapshukov prepared $NaNpO_2CO_{3(s)}$ hydrated solid compounds and characterised them by their X-ray diffraction pattern. $NaNpO_2CO_{3(s)},nH_2O$ (n = 3.5) was obtained in 5 mM to 100 mM Na_2CO_3 solutions. When heated from 30 to 130°C 5 different crystalline phases (n = 3.5, 3, 2, 1, 0) were identified. Their X-ray powder diffraction patterns were reported. The diffraction patterns have many rays, some of them could then correspond to badly crystallised compounds rather than new ones; but this alternative interpretation was not discussed by the authors. There is no way to check this possibility since the structure of the solid compounds was not really identified. In 0.3 to 1.8 M Na_2CO_3 solutions, a $Na_3NpO_2CO_{3(s)}$ hydrated solid was obtained.

[79MOS/POZ]

Moskvin, A.I., Poznyakov, A.N. *Coprecipitation study of complex formation by neptunium(V), plutonium(V), and americium(V) with the anions of various inorganic acids*, Russ. J. Inorg. Chem., 24, 9 (1979) 1357-1362.

Np(V) was coprecipitated with Fe(III) hydroxide in 0 to 0.13 M $NaHCO_3$ aqueous solutions, where the pH was adjusted to 8.5 by adding ammonia or nitric acid. The author interpreted their results with $NpO_2HCO_{3(aq)}$ species ($\log_{10}K_1 = 1.9 \pm 0.1$ at I = 0.25 M and 2.19 at I = 0) essentially because they proposed the formation this species 16 years before [63MOS/GEL]. The influence of $NaHCO_3$, ammonia and nitric acid additions on the solid phase was not controlled. The exact $[CO_3^{2-}]$ cannot be accurately calculated since there is not enough indication about pH calibration, and the ionic strength (I = 0.25?) was probably varying. This review plotted $\log_{10}K_d$ against $\log_{10}[HCO_3^-]$: the 2 or 3 first points show a -2 slope while the 2 last ones a slope of 0. This can be interpreted by a dramatic change in the aqueous Np(V) speciation at $\log_{10}[HCO_3^-] = -1.0$ where the slope change. In this condition $\log_{10}[CO_3^{2-}] = -2.3 \pm 1$: this concentration is consistent with the

$$NpO_2CO_3^- + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$$

equilibrium as predicted by using the formation constants and activity coefficients proposed in this review.

$\log_{10}k_2 = 2.3 \pm 1.0$ in ≈ 0.1 M bicarbonate aqueous solution.

was then estimated by this review from the data of the [79MOS/POZ] publication. This work is then consistent with the Np(V) chemical data selected by this review; but this work was not credited by this review.

[79VOL/TOM]

Volkov, Y.F., Tomilin, S.V., Visyashcheva, G.I., Kapshukov, I.I. *Carbonate compounds of pentavalent actinoids with alkali-metals cations: VI. X-ray structure analysis of $LiNpO_2CO_3$ and $NaNpO_2CO_3$*, Sov. Radiochem., 21, 5 (1979) 579-583. Transl. Radiokhim.,21, 5 (1979) 668-672.

Volkov, Tomilin, Visyashcheva and Kapshukov prepared $MNpO_2CO_{3(s)}$ hydrated solid compounds where M = Li or Na. They characterised them by their X-ray diffraction pattern. $NaNpO_2CO_{3(s)}$ and $LiNpO_2CO_{3(s)}$ (heated up to 250°C) structures were proposed from X-ray powder diffraction study: in these two compounds, the Np atoms would be in NpO_2CO_3 layers that are isostructural to UO_2CO_3 layers in Rutherfordine (UO_2CO_3). In this structure, there are mono and bidentate CO_3^{2-},it is consistent with some infrared work conclusions [73KHA/MOS], but not with a later discussion by the same authors [81VOL/VIS3]. Anyhow, several changes in the structure are possible, and in some of these changes (but not all of them) Na and Np atoms could be exchanged. As in the [77VOL/VIS] publication, crystallographic changes were attributed to temperature effect; but the ageing of the solid in equilibrium with the solution at room temperature, was not studied. The conclusion of this structural study seems reasonable; but it proposed only one of the possible explanation of the powder X-ray diffraction patterns.

[79VOL/VIS]

Volkov, Y.F., Visyashcheva, G.I., Tomilin, S.V., Spiryakov, V.T., Kapshukov, I.I., Rykov, A.G. *Carbonate compounds of pentavalent actinides with alkali metal cations: VII. Synthesis and crystal structure of hydrate compounds with the composition* $Na_{0.6}NpO_2(CO_3)_{0.8}.nH_2O$, Sov. Radiochem., 21, 5 (1979) 583-590. Transl. Radiokhim., 21, 5 (1979) 673-681.

The X-ray diffraction patterns of several $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$ hydrated compounds were reported. Changes in the structure were due to various preparation conditions and treatments. In a later review paper [84VOL/KAP], some of the authors, Volkov and Kapshukov, wrote this compound as $Na_{0.75}(NpO_2)_{1.25}CO_{3(s)}$ (which is exactly the same stoichiometry as $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$). Hydrated $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$ was precipitated from 2 mM bicarbonate solution. Heating this solid, lead to another phase and finally to $NaNpO_2CO_{3(s)}$ solid. x-ray powder diffraction patterns of these solids were observed and calculated. They were interpreted with the structure proposed earlier [79VOL/TOM], which allows continuous variation of Np/Na ratio in the solid. Later solubility study did not confirm this interpretation (see the discussion of the [84VIT] publication in this appendix). Np(V) potentiometric titration with Na_2CO_3 or $NaHCO_3$ solutions presented in this [79VOL/VIS] work, showed evidence of $NaNpO_2CO_{3(s)}$ precipitation and, only in Na_2CO_3 solution, formation of solid or soluble compounds with Np(V)/CO_3^{2-} ratio equal to 2; since the solubility equilibrium was certainly not obtained during the titration, these results should not be used to determine soluble complex stability constants. The important point to select thermodynamic data from solubility measurements, is to find which solid compound is at equilibrium with an aqueous phase. This was not discussed in this work, and it was never confirmed later, that a solid phase with such stoichiometry could control Np(V) solubility. Some of these compounds might well only be metastable phases during the experiments: this review already noticed from the work of this group of authors, that it is difficult to obtain well-crystallised alkaline-Np(V)-CO_3 compounds [74VOL/KAP, 77VOL/VIS]. Later works by this group of authors claimed that this type of compounds had cationic exchange properties; but this was not detected in solubility measurement [84VIT] that could be interpreted with a classical solubility product of fixed stoichiometry.

The author said, that they chose their preparation conditions of their solid compounds, based on results of potentiometric titration of NpO_2^+ aqueous solutions with Na_2CO_3 or $NaHCO_3$. Solid precipitation is often too slow to obtain equilibrium during potentiometric titration that last a reasonable time (less than one day certainly in the present work). The shapes of the three potentiometric titration curves shown in this publication, indicate that the equilibrium was probably not obtained. It would then not be reliable to extract solubility product from that work. The shape and the position of the potentiometric titration curves in potassium (instead of sodium) medium, are not consistent with a previous study by the same group of authors [74VIS/VOL]. The authors did not discuss these points.

For these reasons that work (including the proposed stoichiometry of the solid phases) was not credited by this review.

[79VOL/VIS2]

Volkov, Y.F., Visyashcheva, G.I., Tomilin, S.V., Kapshukov, I.I., Rykov, A.G. *X-ray diffraction analysis of composition and crystal structure of some pentavalent actinide carbonates*, NIIAR-16(375), Dimitrovgrad (1979) 29 p. in Russian.

This report summarises the Volkov's at al. work on the structure of actinide(V) carbonate solid compounds. Most of the information was translated in English in the series of papers published in Soviet Radiochemistry, typically [74VIS/VOL, 74VOL/KAP, 74VOL/KAP2, 76VOL/VIS, 77VOL/VIS, 79VOL/TOM, 79VOL/VIS, 81VOL/VIS, 81VOL/VIS2, 81VOL/VIS3 and 81VOL/VIS4].

[81BIL]

Billon, A. *Sur l'existence de complexes carbonates de Np(V) en solution aqueuse*, in: Techniques for identifying transuranic speciation in aquatic environments, International Atomic Energy Agency, Vienna, 1981, 65-72.

Billon reported Np(V) spectra in 3.2 to 160 mM carbonate / bicarbonate aqueous solutions at pH 7.15 to 11.4. They were not interpreted quantitatively in term of aqueous speciation. There is no indication about pH electrode calibration. It seems that the ionic strength was not constant. A 0.808 mM NpO_2^+ solution did not show any spectral change up to pH = 5.30 in 20 mM bicarbonate solution. This review found that the $NpO_2CO_3^-$ characteristic band [89RIG] appeared, and the NpO_2^+ one was divided by 4.3 at pH = 7.10 in 16 mM bicarbonate solution, where $\log_{10}[CO_3^-] = -4.8$, this review then attributed this spectral change to the

$$NpO_2^+ + CO_3^{2-} \Leftrightarrow NpO_2CO_3^-$$

equilibrium, and calculated

$\log_{10}\beta_1$ = 5.5 ± 0.5 in 16 mM bicarbonate aqueous solution.

In the same way, at pH 9.75 in 8 mM CO_3 solution ($\log_{10}[CO_3^-] = -1.8$) $NpO_2(CO_3)_2^{3-}$ characteristic band [89RIG] appeared and $NpO_2CO_3^-$ one nearly vanished, this review then attributed this spectral change to the

$$NpO_2CO_3^- + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$$

equilibrium, and estimated

$\log_{10}k_2$ > 2.

Another experiment at pH > 11.1, where $[CO_3^{-2}]$ guess is less inaccurate lead to

$\log_{10}k_2$ = 2.5 ± 0.5 in 8 mM carbonate aqueous solution.

$NpO_2(CO_3)_2^{3-}$ characteristic band has a smaller absorbance in 0.16 M than in 0.018 M CO_3 solution, this spectral change can be attributed to the $NpO_2(CO_3)_3^{5-}$ formation [89RIG], and this review then attributed it to the

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

equilibrium, and calculated

$\log_{10}k_3$ = 1.4 ± 1 in 0.16 M carbonate aqueous solution.

These values are not in good agreement with the data selected in this review, probably because $[CO_3^{2-}]$ estimations are wrong (coming from too poor experimental methodology and measurements). This review did not then use that work to select data.

[81VOL/VIS]

Volkov, Y.F., Visyashcheva, G.I., Tomilin, S.V., Kapshukov, I.I., Rykov, A.G. *Study of carbonate compounds of pentavalent actinides with alkali-metal cations: VIII. Synthesis and X-ray diffraction investigation of several compounds of Neptunium(V) with sodium and rubidium*, Sov. Radiochem., 23, 2 (1981) 191-195. Translated from Radiokhim., 23, 2 (1981) 237-242.

Volkov, Visyashcheva, Tomilin, Kapshukov and Rykov prepared $Na_3NpO_2(CO_3)_{2(s)}$, $Na_4NpO_2(CO_3)_{2.5(s)}$, and $Rb_3NpO_2(CO_3)_{2(s)}$ hydrated compounds by precipitation Np(V) in (respectively) 0.3 to 1.7, 2.4 M Na_2CO_3 and 1 to 3.8 M Rb_2CO_3 solutions. The X-ray powder diffraction patterns of these solids were observed and calculated. The authors claimed that they also obtained a $Na_4NpO_2(CO_3)_{2.5(s)}$ solid compound; but the X-ray diffraction pattern shown in their publication could as well be interpreted as a poorly crystallised $Na_3NpO_2(CO_3)_{3(s)}$ hydrated solid compound.

[81VOL/VIS2]

Volkov, Y.F., Visyashcheva, G.I., Tomilin, S.V., Kapshukov, I.I., Rykov, A.G. *Study of carbonate compounds of pentavalent actinides with alkali-metal cations: IX. Determination of the crystal structure of $M_3AnO_2(CO_3)_2.nH_20$*, Sov. Radiochem., 23, 2 (1981) 195-199. Translated from Radiokhim., 23, 2 (1981) 243-247.

This paper is a discussion of previous results by the same group of authors, about $M_3AnO_2(CO_3)_2$ solid compounds. It is confirmed that the structure of this type of solids can change with time. Hydrated $M_3NpO_2(CO_3)_{2(s)}$ (M = Na, K, Rb) crystal structure was proposed; it is not exactly the same as the one proposed for hydrated $NaNpO_2CO_{3(s)}$ [79VOL/TOM]: in Np atom layers all the CO_3^{2-} ions are bidentate, this shift in the structure is then quite different from the ion exchange assumed in $NaNpO_2CO_{3(s)}$ hydrated solids [79VOL/VIS], and this could explain the relatively slow transformation of hydrated $NaNpO_2CO_{3(s)}$ into hydrated $Na_3NpO_2(CO_3)_{2(s)}$ [66GOR/ZEN], but this is not much consistent with [81VOL/VIS3].

[81VOL/VIS3]

Volkov, Y.F., Visyashcheva, G.I., Tomilin, S.V., Kapshukov, I.I., Rykov, A.G. *Study of carbonate compounds of pentavalent actinides with alkali-metal cations: X. Composition and crystal structure of carbonates*, Sov. Radiochem., 23, 2 (1981) 200-204. Translated from Radiokhim., 23, 2 (1981) 248-253.

This paper is an attempt to give a structural explanation of the formation of potassium Np(V) carbonate compounds previously prepared by this group of author [74VIS/VOL, 74SIM/VOL, 74VOL/KAP, 74VOL/KAP2, 77VOL/VIS, 79VOL/TOM, 79VOL/VIS, 81VOL/VIS and 81VOL/VIS2]. $NaNpO_2CO_{3(s)}$ was no more proposed to be isostructural to the Rutherfordine [79VOL/VIS]; but there is no experimental evidence for this new interpretation. The general explanation of the structure changes seems reasonable; but some of the results used were not really confirmed. The author assumed the possibility of ionic exchange with continuous variations of some lattice parameters. It seems that they might have sometime interpreted some of their results to support this interpretation, a bit too quickly, without checking whether any of the proposed solid compounds were kinetic artefact. No attempt was made to check whether the mass action law could account for this type of ionic exchange. Only one possible non stoichiometric compound was proposed [79VOL/VIS]; but this study was not completely convincing (see [84VIT] and the discussion of the [79VOL/VIS and 84VIT] publications in this appendix). Later Np(V) solubility study in sodium carbonate / bicarbonate media showed no evidence of non-stoichiometric compounds. For these reasons, this review did not consider that the discussion proposed in this paper, was supported by enough experimental verifications. The author mentioned the $K_4NpO_2(CO_3)_{2.5(s)}$ solid compound; but it does not seem that it X-ray diffraction pattern was published, and the corresponding sodium (instead of potassium) compound was not clearly characterised neither (see the discussion of [81VOL/VIS] in this appendix).

[81VOL/VIS4]

Volkov, Yu.F., Visyashcheva, G.I., Tomilin, S.V., Kapshukov, I.I., Rykov, A.G. *Study of carbonate compounds of pentavalent actinides with alkali-metal cations: XI. Ion-exchange properties of the carbonates of Np(V), Pu(V) and Am(V)*, Sov. Radiochem., 23, 2 (1981) 205-209. Translated from Radiokhim., 23, 2 (1981) 254-258.

This work is an extension of the previous one [81VOL/VIS3], for the exchange of new cation with Actinyl(V) ones. As for this previous publication, [81VOL/VIS3], this review did not consider that the discussion proposed in this paper, was supported by enough experimental verifications.

[83MAY]

Maya, L. *Hydrolysis and carbonate complexation of dioxoneptunium(V) in 1.0 M $NaClO_4$ at 25°C*, Inorg. Chem., 22 (1983) 2093-2095.

Table [83MAY]: Curve fitting results of Maya's solubility measurements of Np(V) in $Na^+/CO_3^{-2}/HCO_3^-$ media. $\log_{10}$ of the equilibrium constants (named in the first column) are tabulated. $K_{s1} = [Na^+]\,[NpO_2^+]\,[CO_3^{-2}]$, is a hydrated $NaNpO_2CO_{3(s)}$ solubility product. $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2^+]\,[CO_3^{-2}]^i)$, ${}^*\beta_i = [NpO_2OH_{(aq)}]\,[H^+] / [NpO_2^+]$. Σ is the standard deviation calculated in the same way by this review, for all the data tabulated here. Fitting by this review minimised it (two last columns). w. mean = weighted mean. For w. mean1, the weight was the (calculated theoretical error) / (minimum error) ratio, while it is the percentage of the species (for which the formation constant was calculated) in the w. mean2 calculation. In both cases, uncertainty is 1.96 (standard deviation) of the corresponding weighted mean. The proposed values (bolded) were obtained by curve fitting with fixed values for the hydrolysis formation constants. There was not enough experimental data to rely on the statistical determination of the uncertainty which have been increased for the solubility product and the $NpO_2CO_3^-$ formation constant to account for possible poor equilibrium achievement.

	[83MAY]	Calculated by this review from the result of [83MAY]			
		w. mean1	w. mean2	best fit	**Proposed values**
K_{s1}	-10.14 ± 0.04	-10.13 ± 0.24	-10.11 ± 0.15	-10.14	**-10.12 ± 0.35**
β_1	4.49 ± 0.06	4.56 ± 1.00	4.56 ± 0.15	4.56	**4.57 ± 0.35**
β_2	7.11 ± 0.07	7.13 ± 0.30	7.04 0.24	7.05	**7.03 ± 0.24**
β_3	8.53 ± 0.09	8.54 ± 0.40	8.44 ± 0.41	8.53	**8.52 ± 0.41**
${}^*\beta_1$	-9.12 ± 0.15	-11[a]	-11[a]	-9.47	-11[a]
${}^*\beta_2$		-23[a]	-23[a]	-26.74	-23[a]
1.96 Σ	0.104	0.110	0.100	0.090	0.097
$K_{s1}\ \beta_1$	-5.65	-5.57	-5.55 ± 0.15	-5.58	**-5.55 ± 0.35**
$K_{s1}\ \beta_2$	-3.03	-3.00	-3.07 ± 0.24	-3.09	**-3.10 ± 0.24**
$K_{s1}\ \beta_3$	-1.61	-1.59	-1.66 ± 0.41	-1.61	**-1.60 ± 0.41**
β_2 / β_1	2.62	2.57	2.44 ± 0.06	2.50	**2.45 ± 0.26**
β_3 / β_2	1.42	1.41	1.42 ± 0.36	1.48	**1.50 ± 0.36**

[a] non fitted (= fixed) value.

After Simakin's paper in 1977 [77SIM] that established the stoichiometry of the Np(V) carbonate limiting complex, this is the first reliable work from which the stability of the soluble carbonate complexes was calculated. This review used this experimental work and followed most of the interpretation of the author to select thermodynamic data. There are still several chemical problems that are not clearly explained in this publication (see below). The author was probably aware of most of them since the experimental work and its interpretation were correct. Maya measured the Np(V) solubility in carbonate / bicarbonate aqueous solutions at $8.08 < -\log_{10}[H^+] < 10.99$. The glass electrode was correctly calibrated in concentration units ($-\log_{10}[H^+]$ and not pH). The solid was precipitated, and aged during 8 days. Its Np(V) / carbonate ratio = 1 was deduced from chemical analysis. Maya measured the solubility in batches, in some of them he added CO_2 gas before a second solubility measurement. This methodology should allow to make the difference between carbonate complexation and hydrolysis; the $NpO_2OH_{(aq)}$ formation constant proposed by the author is overestimated in comparison of future work selected by this review, and anyhow the $NpO_2OH_{(aq)}$ contribution to the Np(V) solubility calculated with Maya's formation constant, were always less than the uncertainty. The difference between the two sets of data (before and after CO_2 bubbling) could as well be attributed to the ageing of the solid. Maya said that its solid phase, $NaNpO_2CO_{3(s)},3.5H_2O$, was characterised by X-ray diffraction; but later work (see the discussion of [84VIT] in this appendix) indicated that the comparison of the X-ray diffraction pattern with the published ones for such compounds, is not straightforward, probably due to the difficulty to obtain equilibrium prior to solubility measurements. The author did not discuss this points which could mean that he did not realise it. He did not obtain enough experimental data to check their scattering; but as discussed above, the difference between the two sets of results (at different CO_2 partial pressures and times) could then be attributed to the scattering of the data typically due to ageing of the solid phase (see the discussion of [84VIT] in this appendix). Maya interpreted his solubility data with the following equilibria

$$NaNpO_2\,CO_{3(s)} \Leftrightarrow Na^+ + NpO_2^+ + CO_3^{-2}$$
$$NpO_2^+ + i\,CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_i^{1-2i}$$
$$NpO_2^+ + OH^- \Leftrightarrow NpO_2OH_{(aq)}$$

and calculated the corresponding formation constants. This review followed this interpretation and found practically the same formation constants; but there was practically only one experimental solubility measurement in chemical conditions where the limiting complex was predominating. Maya determined the CO_3^{-2}/HCO_3^- and the HCO_3^-/CO_2 acidic constants,

$\log_{10}{}^*K_1$ = 9.55 ± 0.02 [83MAY], 9.59 ± 0.05 (this review)
$\log_{10}{}^*K_2$ = 6.03 ± 0.004 [83MAY], 6.13 ± 0.05 (this review)

The $\log_{10}{}^*K_1$ value determined by Maya is consistent (within the uncertainty) with the value calculated with the auxiliary data used by this review, and zero ionic strength, the SIT coefficients and the corresponding error propagation. There is no reason to change Maya's ${}^*K_1$ value. The $\log_{10}{}^*K_2$ value determined by Maya is not consistent with the data used by this review; but this had negligible effect on the $[CO_3^{-2}]$ determination and the Np(V) results. Still, this review recalculated the total carbonate concentration as indicated in the [83MAY] publication with Maya's ${}^*K_i$ values, and then shifted Maya's $-\log_{10}[H^+]$ by 0.04 $\log_{10}$ unit (to account for the influence of the difference in the ${}^*K_1$ value, during the glass electrode calibration) and calculated back the carbonate speciation with the ${}^*K_i$ value used by this review. Curve fitting of the Np(V) solubility data gave the same results with both set of ${}^*K_i$ values. Using all Maya's value, this review calculated the solubility product and complexation constants in different ways (see the table) which all gave the same results (within uncertainty). This review ploted the error

$$e = \log_{10}[Np(V)]_{calculated} - \log_{10}[Np(V)]_{measured}$$

as a function of $\log_{10}[OH^-]$, $\log_{10}[CO_3^{-2}]$, $\log_{10}[HCO_3^-]$ or $\log_{10}P_{CO2}$. No systematic deviation could be detected. In contradiction with Maya's proposition, this review estimated that the hydrolysis formation could not be fitted and checked that their possible values had no influence on the results. This is consistent with the fact that e and $\log_{10}[OH^-]$ were practically not correlated.

Ionic exchange within the solid phase, or change in the solid phase to obtain a non-stoichiometric one was suggested by Volkov's series of publication (see the discussion of the [79VOL/VIS and [81VOL/VIS4] publications in this appendix); but this was not confirmed by the analysis of Maya's solubility data, where no evidence of correlation between e and $\log_{10}[CO_3^{-2}]$, was found (see the discussion of the [84VIT] publication for more explanation on this assumption). For the same reason, as suggested by later work (see the discussion of the [84VIT] publication in this appendix), the scattering of the data was certainly mainly due to poor crystallisation of the solid phase, specially in the chemical conditions were NpO_2^+ or $NpO_2CO_3^-$ are the predominating species. For this reason, the uncertainty of the corresponding equilibrium constants was arbitrary increased by this review. Only minor criticisms can be pointed out about this work:

1 - $NaNpO_2CO_{3(s)}$,$3.5H_2O$ might not be so well characterised because several complicated X-ray diffraction patterns of general formula $NaNpO_2CO_{3(s)}$,xH_2O or $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$,$xH_2O$ were published [81VOL/VIS3] which indicates that good crystallisation is difficult to obtain, there are too few experimental points to know from statistical error analysis whether solubility product law was well verified (solid phase equilibration, and see 2) ;

2 - X-ray analysis was performed before and not after solubility equilibration, solid phase transformation during the equilibration of the initial solid with the aqueous solution could not then be detected, comparing this work with a similar one with much more experimental points [84VIT and 86GRE/ROB] indicates that this type of phenomenon is possible (see also the discussion of the [84MAY] publication in this appendix), and also a hydrated $Na_3NpO_2(CO_3)_{2(s)}$ is the thermodynamic stable phase when $[CO_3^{2-}]>0.01$ M ;

3 - too few experimental points are presented to perform a proper statistical error analysis ;

4 - the sensitive analysis was based on the fact that solubility is practically only $[CO_3^{2-}]$ dependent even when the carbonic gas partial pressure was varied within the same batch. This procedure is a proper methodology but the way it is used is not much convincing for 2 reasons :

4.1 - $[CO_3^{2-}]$ and $[HCO_3^-]$ calculations from $-\log_{10}[H^+]$ measurements have certainly been properly done, but the author did not give any explanation about them, their are not straight forward since solubility have first been measured in Na_2CO_3 solutions where P_{CO2} was low ($10^{-4.7}$ to 10^{-6} atm calculated by this review), 1 per cent CO_2 gas (in nitrogen) was then bubbled through the batches before new solubility measurements, then one expects an increase of the total carbon in the solution due to the

$$CO_3^{2-} + CO_{2(g)} \Rightarrow 2\ HCO_3^-$$

reaction. This assumption was verified by this review ($[HCO_3^-]_{final}$ is not far from $2\ [CO_3^{2-}]_{initial}$) which indicates that $[CO_3^{2-}]$ and $[HCO_3^-]$ calculations from $-\log_{10}[H^+]$ measurements should have been properly done, it was also verified that $-\log_{10}[H^+]$ measurements in the batches where CO_2 had been bubbled was consistent with this interpretation;

4.2 - the above procedure (4.1) produced experimental points at low $-\log_{10}[H^+]$ and $[CO_3^{2-}]$ together, there is then no sensitivity analysis for the $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ formation;

5 - solubility measurements (with a single solid phase) cannot detect polynuclear complexes.

But, as stated above, this review used this work since there is later evidence that Maya's interpretation was correct and because there are very few works in this field, based on correct experimental procedure, especially correct pH measurements.

[84MUL/GOR]

Mulac, W.A., Gordon, S., Schmidt, K.H., Wester, D., Sullivan, J.C. *Reactions of uranium(V), neptunium(V), and plutonium(V) with the carbonate radical ion*, Inorg. Chem., 23 (1984) 1639-1641.

In the course of this kinetic work, Mulac et al. measured the redox potential of the An(VI)/An(V) couple by cyclic voltametry in Na_2CO_3 aqueous solution for An = U, Np and Pu. The actual Na_2CO_3 concentration was not clearly reported, it probably was 0.05 M. There is no indication on the junction potential. For these reasons, this review did not use the data reported in this work. The An(VI)/An(V) couple was also written $AnO_2(CO_3)_3^{-4}$ / $AnO_2(CO_3)_3^{-5}$ in this publication, which is correct in concentrated Na_2CO_3 aqueous solution; but in 0.05 M Na_2CO_3 aqueous solution the dissociation of the An(V) limiting complex should probably not be neglected.

[84VAR/BEG]

Varlashkin P.G., Begun G.M., Hobart D.E. *Spectroscopic and electrochemical investigations of neptunium and plutonium in concentrated aqueous carbonate and carbonate-hydroxide solutions*. DOE/ER/04447-168 (Dec. 1984) 5-13.

This is a previous report of the [84VAR/HOB] publication. Varlashkin, Begun and Hobart prepared Np(V) complexes in concentrated Na_2CO_3 aqueous, and measured the absorption spectra of the solution after NaOH additions to obtain 0.02, 0.38 and 1.3 M NaOH aqueous solution. The Na_2CO_3 concentration was not clearly indicated, it was probably 2 M, when an excess of Np(V) was used to obtain a solid compound, that was identified by X-ray diffraction, to be the $Na_3NpO_2(CO_3)_{2(s)}$ hydrated compound. The authors did not interpret these spectral changes. They were confirmed later [89RIG] and interpreted as an evidence of the formation of mixed Np(V)-CO_3-OH complex(es).

[84VAR/HOB]

Varlashkin P.G., Hobart D.E., Begun G.M., Peterson J.R. *Electrochemical and spectroscopic studies of neptunium in concentrated aqueous carbonate and carbonate-hydroxide solutions*. Radiochim. Acta, 35 (1984) 91-96.

see [84VAR/BEG].

[84VIT]

Vitorge P. *Measurements of Thermodynamic Constants of Transuranic Compounds to Predict their Geochemistry: Carbonate Complexation of Np(V) and Am(III), Hydrolysis of Pu(VI) and Am(III).* In French. Séminaire sur les techniques d'étude et les méthodes d'évaluation des sites en vue du stockage définitif des déchets radioactifs IAEA-SR-104/25. Sofia, Bulgaria (6-10 February 1984).

This conference paper reports many experimental results on figures, their interpretation on figures and in tables, and literature comparison and reinterpretations. The experimental data were preliminary results. Those concerning Np(V) in carbonate media are discussed elsewhere in this appendix (see the discussion of the [86GRE/ROB and 89RIG] publications in this appendix). Np(V) was precipitated in $NaHCO_3$ aqueous solution. The solid compound was equilibrated in this aqueous solution at constant ionic strength (3 M $NaClO_4$) under CO_2 bubbling. The pH was decreased and increased, so that Np(V) solubility measurements (over more than 3 orders of magnitude) were obtained from both dissolution and precipitation. The experimental results were reasonably reproducible, but they were more scattered (about 0.4 $\log_{10}$ unit) at the minimum solubility (a few µM Np(V)), than in more acidic media (about 0.2 $\log_{10}$ unit), that were also more scattered than in more basic solution as published later [86GRE/ROB and 89RIG]. The author said that this problem was correlated with a few extra lines in the X-ray diffraction patterns. One of these X-ray diffraction patterns was identical to a previously published Na-NpO_2-CO_3 one [79VOL/VIS]. This Na-NpO_2-CO_3 compound had been prepared by heating at 350°C a compound that was assumed to be initially $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$ [79VOL/VIS]. Vitorge then tested two interpretations of his solubility measurements. In one of them the solid phase was assumed to be hydrated $Na_{0.72}NpO_2(CO_3)_{0.86(s)}$, while in the other one it was hydrated $NaNpO_2CO_{3(s)}$. Both models were consistent with the experimental results, and slope analysis shown on figures of this publication cannot distinguish between them. This certainly indicates that at least some of the solid compounds prepared by Volkov's group were simply poorly crystallised, that equilibrium conditions were not obtained. Finally the formation of the corresponding compounds proposed by Volkov's were then not proven. These compounds were supposed to be ionic exchanger corresponding then to the

$$2\ (x\text{-}1)\ Na^+ + NaNpO_2CO_{3(s)} \Leftrightarrow Na_{2x\text{-}1}NpO_2(CO_3)_{x(s)} + (1\text{-}x)\ CO_3^{-2}$$

ionic exchange equilibrium. At constant Na^+ concentration (as in the present [84VIT] work), and for x < 1 as assumed by Volkov et al., the non-stoichiometric solid phase is expected to be stabilised by decreasing the CO_3^{-2} concentration, if one assumes that x can vary. Vitorge's interpretation and figures of the [84VIT] publication indicated that over a wide chemical domain ($-9 < \log_{10}[CO_3^{-2}] < -4.5$), the $\log_{10}[Np(V)]_{total}$ vs. $\log_{10}[CO_3^{-2}]$ variations are linear with slope -x, where x fitted value were 0.86; but were x = 1 were still within the uncertainty. Whatever the -x value was, it is the slope of the straight line which can then be assumed to be practically constant, while Volkov et al.'s interpretation suggested that in the above ionic exchange x could vary. This is not much consistent or this means that x variations are too small to be detected. So, as for Maya's previous publication [83MAY], solubility measurements did not show evidence of ionic exchange within the solid as proposed by Volkov et al.. This indicates that there is no need to take into account this ionic exchange process, if it exists, when this type of solid phases is equilibrated with aqueous solution.

The author calculated the formation constant of the $NpO_2(CO_3)_i^{-2i+1}$ soluble complexes, extrapolated them to zero ionic strength, compared them with published data that they also reinterpreted (see the discussion of [89RIG] in this appendix).

[84VOL/KAP]

Volkov, Y.F., Kapshukov, I.I., A.G. *Some aspects of the crystal chemistry of actinides in higher oxidation states*, Sov. Radiochem., 26, 3 (1984) 341-349. Translated from Radiokhim., 26, 3 (1984) 361-370.

[85BID/TAN]

Bidoglio, G., Tanet, G., Chatt, A. *Studies on neptunium(V) carbonate complexes under geologic repository conditions*, Radiochim. Acta, 38 (1985) 21-26.

A liquid-liquid extraction technique was used to measured the Np(V) carbonate complex formation constants. Np(V) have been used at a concentration lower than solubility or spectrophotometric detection limit; but the chemical system is quite complicated. The pH was controlled with a buffer (TRIS) that should not interfere, the extractants (TOMA and TTA) were involved in side reactions, that were taken into account (but it is difficult to do it accurately and to be sure that none of them have been forgotten). This review estimated that when no carbonate was added, there was no evidence of $NpO_2OH_{(aq)}$ formation (compared with possible side reactions) up to pH = 9.2 then

$$\log_{10}{}^*K_1 \quad << \quad -9.2,$$

the value fitted by the authors, $\log_{10}K_1 = 4.16$ (that should correspond to $\log_{10}{}^*K_1 = -9.84$ assuming that the author has calculated ${}^*K_1$ from pH measurements by using $\log_{10}K_w = -14.00$) was then probably a mathematical fitting artefact. The authors used these experiments to study the

$$NpO_2^+ + i\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_i^{1-2i}$$

equilibria for i = 1 and 2 ($NpO_2(CO_3)_3^{-5}$ was not detected), which is perfectly correct. For $0.1 < [CO_3^{2-}] < 1$ mM, with $0.4 < [CO_3]_t < 10$ mM (in HCO_3 medium where 8.2 < pH < 9.0) the predominant species was found to be $NpO_2(CO_3)_2^{3-}$ (which is consistent with the values selected by this review) and the value of its formation constant proposed by the author(see the table) fitted reasonably well (see below) the experimental results. The $NpO_2CO_3^-$ formation constant calculated by the author, 4.14, does not seem to fit well the results shown on the figures of this publication, this review rather estimated 3.9 by using the same graphical method as the author. Anyhow both values over-estimate the $NpO_2CO_3^-$ stability (compared with the value selected by this review from other experimental works) which can merely be due to a side reaction. An extra experiment in 0.1 M $NaClO_4$, 0.1 M $NaHCO_3$ solution does not fit well the results, and this review followed the author when he said that this inconsistency could hardly be attributed to the formation of the $NpO_2(CO_3)_3^{5-}$ limiting complex. Several $[CO_3^{2-}]$ and pH has been used and varied independently, hence, since the results could be plotted

Table [85BID/TAN, 85INO/TOC] : Curve fitting results of Np(V) carbonate complexing constants from liquid-liquid extraction measurement of the [85BID/TAN] and [85INO/TOC] publications. $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2^+][CO_3^{2-}]^i)$. Σ is the standard deviation calculated (by this review). The data of the [85BID/TAN] publication is tabulated in the first line, for this line, the β_3 value were evaluated from an independent set of measurements that were not used to fit β_1 and β_2, neither to estimate their uncertainty (2σ) in the [85BID/TAN] publication. In the following lines (except the bolded one) the uncertainty is 1.96σ calculated on all the 71 (weighted) experimental data, when no uncertainty is indicated, the corresponding β_i was not fitted, it was fixed to the value calculated from the thermodynamic data selected by this review (from other experimental measurements). These formation constants were not considered by this review (see the text). The reinterpretation finally proposed by this review, is bolded, the uncertainty takes into account possibly systematic error (see the text). For comparison the curve fitting results from the data of the [85INO/TOC] publication are also tabulated.

	I	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	1.96 Σ
0.1M $NaClO_4$ [85BID/TAN]	0.2	4.13 ± 0.03	7.06 ± 0.05	< 9	0.27
this review for the uncertainty, [85BID/TAN]	0.2	4.13 ± 0.01	7.06 ± 0.04	9 ± 2.12	0.27
this review	0.2	4.48	6.60	7.22	0.67
3 fitted β_i by this review from [85BID/TAN]	0.2	4.019 ± 0.008	$6.45_0 \pm 0.11_4$	9.51 ± 2.64	0.11
2 fitted β_i by this review from [85BID/TAN]	0.2	$3.80_0 \pm 0.05_5$	$7.22_5 \pm 0.05_7$	7.22	0.18
proposed by this review from [85BID/TAN]	**0.2**	**3.80 ± 0.36**	**7.22 ± 0.78**		
1M $NaClO_4$ [85INO/TOC]	1	4.14 ± 0.01	6.78 ± 0.01		0.077
this review for the uncertainty, [85INO/TOC]	1	4.14 ± 0.05	6.78 ± 0.005		0.077
this literature review	1	4.55	7.06	8.62	0.485
fitted β_i by this review from [85INO/TOC]	1	$4.11_5 \pm 0.05_6$	$6.81_3 \pm 0.003$	8.65	0.076
proposed by this review from [85INO/TOC]	**1**	**4.14 ± 0.5**	**6.78 ± 0.5**		

against $[CO_3^{2-}]$ on a unique curve, the predominant complexes contained only CO_3^{2-} ligand. The authors have used a classical graphical method to interpret their data; but this review also used another one: the data from the figures 4 and 6 of the [85BID/TAN] publication was scanned, and $\log_{10}D/D°$ vs.. $\log_{10}[CO_3^{2-}]$ was then plotted on a single figure, and compared with theoretical curves calculated with fitted complexing constants (see the table). The experimental data were never scattered at random (about the theoretical curve): this is an evidence of systematic error. In this representation; the value of the slopes ($\log_{10}D/D°$ / $\log_{10}[CO_3^{2-}]$) measured from the experimental data, were always a little less than the theoretical one, and it was not possible to find a set of complexing constants that could avoid this systematic deviation. This systematic deviation was then confirmed by statistical analysis. This review considered, that there was an unknown chemical problem in this liquid-liquid extraction system. For this reason the data of this publication were disregarded.

[85COM]

Côme B. (Edited by) MIRAGE project. First summary report (1983). EUR 9543 (1985).

This report includes a summary of works performed for several European (CCE) contracts. The names of the main authors of these summaries only appear in the text. P. Vitorge and co-workers' work for the WAS 83-361.7 contract (P. Vitorge, J. Oliver, J.P Mangin, A. Billon. *Solubility and Speciation of Np and Pu in Groundwaters.* Study of the Physico-Chemical Properties on the Transuranian Elements in Connection with the Migration Phenomenon in the Geosphere) was summarised by Kim. Preliminary values of equilibrium constants (page 20 of [85COM]) were reported for the formation constants of the soluble carbonate complexes $NpO_2(CO_3)_i^{1-2i}$ where i = 1, 2 and 3, and for the solubility products of hydrated $Na_{2i-1}NpO_2(CO_3)_{i(s)}$ where i = 1 and 2. Equilibrium constants from the same set of experimental data were published by Vitorge et al. before [84VIT] and later [85KIM, 86GRE/ROB, 89RIG] with more information and figures: see the discussion of the [89RIG] publication in this appendix.

[85INO/TOC]

Inoue, Y., Tochiyama, O. *Studies of the complexes of Np(V) with inorganic ligands by solvent extraction with thenoyltrifluoroacetone and 1,10-phenanthroline. I. Carbonato complexes*, Bull. Chem. Soc. Jpn., 58(2) (1985) 588-591.

Inoue and Tochiyama studied Np(V) carbonate complexes in 1M $NaClO_4$ aqueous solutions, with a liquid-liquid extraction technique. They determined formation constants that are not in accord (within uncertainties estimated by the authors) with a previous solubility study [83MAY] in the same medium. Since there was no information about the procedure to calibrate the glass electrode, this review increased the uncertainty by 0.5 unit $\log_{10}$. The results of both publications [83MAY and 85INO/TOC] were then consistent. Inoue and Tochiyama [85INO/TOC] performed work similar to Bidoglio, Tanet and Chatt's (see the discussion of the [85BID/TAN] publication in this appendix). The authors interpreted their data with

$$NpO_2^+ + i\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_i^{1-2i}$$

equilibria for i = 1 and 2 ($NpO_2(CO_3)_3^{-5}$ was not detected), which is correct. The 71 Bidoglio, Tanet and Chatt's experimental data [85BID/TAN] were more scattered than the 101 Inoue and Tochiyama ones [85INO/TOC]. In contradiction with the systematic deviation found by this review in the experimental data of the [85BID/TAN] publication (see the discussion of this publication in this appendix), theoretical $\log_{10}D$ vs.. $\log_{10}[CO_3^{-2}]$ curves fitted reasonably well the experimental data reported in the in the present work [85INO/TOC]. This review scanned the figure 2 of the [85INO/TOC] publication and performed curve fitting to determined the $NpO_2(CO_3)_i^{1-2i}$ formation constants. They were consistent (within uncertainties) with those initially proposed by the authors. Since the scanning procedure could add supplementary error, this review used Inoue and Tochiyama data; but their uncertainty was increased by 0.5 unit $\log_{10}$. (as explained above). It was then confirmed that the formation constants determined in this liquid-liquid extraction study are less accurate than the ones previously determined in a [83MAY] solubility work. Both works were consistent only because this review increased the uncertainty of the liquid-liquid extraction results [85INO/TOC] for possible error in pH calibration (as explained above). For this reason, these results were not used by this review to select thermodynamic data.

[85KIM]

Kim J.I. *Basic Actinide and Fission Product Chemistry.* in MIRAGE project. Second summary report (1984) edited by Côme B. EUR 10023 (1985).

This report includes a summary of works performed for several European (CCE) contracts. As for the [85COM] report, Kim summarised the work of other authors on Np(V) chemistry in carbonate / bicarbonate media: see the discussion of the [89RIG] publication, and of the [85BID/TAN] one in this appendix, for the data of Vitorge and of Bidoglio's group respectively.

[86GRE/ROB]

Grenthe I., Robouch P., Vitorge P. *Chemical Equilibria in Actinide Carbonate Systems*. Actinide 85. Aix-en-Provence. J. Less. Common Metals, 122, 255-31 (1986).

In this publication, solubility products, and formation constants of soluble complexes were deduced from Np(V) solubility measurements in bicarbonate / carbonate aqueous solutions at high ionic strength (3 M $NaClO_4$). Using published data at lower ionic strength, extrapolation to zero ionic strength and SIT coefficients were proposed. Preliminary experimental results and interpretation appeared in the [84VIT, 85COM and 85KIM] publications. This work [86GRE/ROB] is discussed in this appendix with the [89RIG] thesis. Qualitatively, this experimental work showed that

1 Np(V) major soluble species contain only carbonate ligand for $0.1 < pCO_2 < 1$ atm or in carbonate / bicarbonate buffers;

2 $NpO_2(CO_3)_3^{5-}$ limiting complex is stable only at high ionic strength;

3 $NaNpO_2CO_{3(s)}$ hydrated solid was not well precipitated at low carbonate concentration ($lg[CO_3^{2-}]<-3.5$), it is stable and well crystallised in oversaturated solutions ($1mM < [CO_3^{2-}] < 0.1mM$) where $Na_3NpO_2(CO_3)_{2(s)}$ hydrated solid precipitated slowly.

[87LEM/BOY]

Lemire,-R.J.; Boyer,-G.D. *The solubilities of sodium dioxoneptunium(V) carbonate hydrates at 30, 50 and 75°C.* International conference on chemistry and migration behaviour of actinides and fission products in the geosphere (Migration '87). Muenchen (Germany, F.R.). 14-18 Sep 1987. Abstracts. 1987. 196 p. p. 82-83. Technische Univ. Muenchen, Garching (Germany, F.R.). Inst. fuer Radiochemie.

See [93LEM/BOY].

[89RIG]

Riglet Ch. *Chimie du neptunium et autres actinides en milieu carbonate*. Thèse Université Paris 6. 17/3/1989, 267p. see also [90RIG and 91RIG/VIT]

The experimental methodologies and the interpretation used in this thesis were correct. The aqueous speciation was controlled at constant ionic strength ($NaClO_4$ media) by $CO_{2(g)}$ / HCO_3^- or HCO_3^- / CO_3^{-2} buffers, bubbling carbonic gas in an open cell, or in closed batches respectively. For potentiometric measurements the junction potentials could be neglected because the same ionic medium (typically 3 M $NaClO_4$) was used for the working solution and the reference electrode one, and glass electrodes were calibrated in concentration units, in the same ionic medium as the working solutions. Auxiliary thermodynamic data used for $-\log_{10}[H^+]$ calibration were consistent with those used by this review.

The formation of Np(V) carbonate soluble complexes in carbonic / bicarbonate / carbonate aqueous solutions were studied by spectrophotometry (pages 140 to 151 of this thesis). $NpO_2CO_3^-$ formation constant was measured in $NaClO_4$ 0.5 M bicarbonate solution at $pCO_2 = 1$ atm, by using absorptivity at 991 nm, and 2 different Np(V) concentrations (0.460 and 0.195 mM), which confirmed that this complex is not polynuclear. This is a good methodology to determine the $NpO_2CO_3^-$ formation constant, β_1, since there are no systematic errors as in solubility techniques (see below), and there is not too much overlapping of the characteristic picks of the two Np(V) species. This review checked graphically the β_1 value on figures (page 141 of [89RIG]) and recalculated it from the absorbance measured at 981 nm (tabulated page 225) corresponding to a NpO_2^+ pick to minimise interferences with the $NpO_2(CO_3)_2^{3-}$ formation. The β_1 values determined by Riglet or by this review are in accord (with uncertainties) and reasonably accurate (see the table). They are consistent with the value selected by this review, and with later studies as reinterpreted by this review [90NIT/STAN and 94NEC/KIM] that reproduced Riglet's measurements (but at lower ionic strength). Main uncertainty was due to the influence of the second carbonate complex, $NpO_2(CO_3)_2^{3-}$. This influence was rather small (as explained above), and explained the small difference between the two determinations and curve fitting (see below). The value estimated for β_1 by this review was used by this review to select thermodynamic data extrapolated to zero ionic strength. The molar absorptivity of the $NpO_2CO_3^-$ pick at 991 nm were found to be 300 $mol.^{-1}.cm^{-1}$. There is no doubt about the stoichiometry of this complex; but it is similar to the pick attributed to $NpO_2OH_{(aq)}$ in the [76SEV/KHA] publication. $NpO_2(CO_3)_2^{3-}$ was hardly detected in these conditions. Anyhow, as explained above, this $NpO_2CO_3^-$ pick at 991 nm was not used by the present review since interference with $NpO_2(CO_3)_2^{3-}$ formation was more important at this wavelength.

The Np(V) spectral variations at 998 nm (there is a $NpO_2(CO_3)_2^{3-}$ pick at this wavelength) for $0.02 < [CO_3^-] < 0.4$ at different ionic strengths (0.5 to 3 M) were used to measured the stepwise formation constant, k_3, of the

$$NpO_2(CO_3)_2^{3-} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-}$$

equilibrium and the corresponding

$$\Delta\varepsilon_3 = \varepsilon(NpO_2(CO_3)_3^{5-}, Na^+) - \varepsilon(NpO_2(CO_3)_2^{3-}, Na^+) - \varepsilon(CO_3^{2-}, Na^+) \qquad = -0.14 \pm 0.10 \text{ kg/mole.}$$

In the same experiments, spectral variations at 990 nm were used to measure the stepwise formation constant, k_2, of the

$$NpO_2CO_3^- + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_2^{3-}$$

Table [89RIG]1: Experimental conditions of the [89RIG] publication spectrophotometric measurement.

series n°	$[NaClO_4]_{initial}$ (M)	$[Na_2CO_3]_{initial}$ (M)	$[Np(V)]_{total}$ (mM)	$\log_{10}[CO_3^{2-}]$ range
1	0.5	0	0.046	< -4.3
2	0.5	0	0.0195	-2.06 to -0.4
3	0.5	0	0.0218	-1.4 to -0.6
4	1	0	0.0109	-1 to -1.8
5	2	0	0.0109	-2
6	3	0	0.0054	-1.6 and -1.7
7	0	0.13 to 2	1.08	-0.89 to 0.30
8	0	0.01 to 0.1	0.2	-2 to -1

Table [89RIG]2: Np(V) carbonate complexing constants deduced from the spectrophotometric measurement of the [89RIG] publication. $k_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2(CO_3)_{i-1}^{3-2i}] [CO_3^{2-}])$. The equilibrium constants deduced from only a part of the experimental data are italicisized to stress that they were not used by this review.

	I	medium	$\log_{10}k_1$	$\log_{10}k_2$	$\log_{10}k_3$
series 7 and 8	0				*-0.98 ± 0.15*
series 4 to 6	0			*1.51 ± 0.15*	*-0.86 ± 0.15*
data finally proposed in [89RIG]	0		4.7 ± 0.2	1.51 ± 0.15	-0.86 ± 0.15
this review	0.12	Na_2CO_3		1.4 ± 0.3	
this review	0.17	Na_2CO_3			1.0 ± 0.28
series 1	0.5	$NaClO_4$	*4.30 ± 0.10*		
series 2	0.5	$NaClO_4$	*4.41*	*3.35*	
series 1 and 2	0.5	$NaClO_4$	*4.75*	*3.71*	
this review series 7 and 8	0.18	Na_2CO_3			*0.90 ± 0.2*
series 4 to 6	0.5	$NaClO_4$		*2.23 ± 0.07*	*1.37 ± 0.07*
data finally proposed in [89RIG]	0.5	$NaClO_4$	4.3 ± 0.1	2.23 ± 0.07	1.37 ± 0.07
this review	0.5	$NaClO_4$	4.41 ± 0.1	2.1 ± 0.6	1.13 ± 0.2
series 7 and 8	1	Na_2CO_3			*1.60 ± 0.07*
series 4 to 6	1	$NaClO_4$		*2.38 ± 0.07*	*1.86 ± 0.07*
data finally proposed in [89RIG]	1	$NaClO_4$	4.3 ± 0.2	2.38 ± 0.07	1.86 ± 0.07
this review	1	$NaClO_4$			1.48 ± 0.2
series 7 and 8	2	Na_2CO_3			*2.05 ± 0.07*
series 4 to 6	2	$NaClO_4$		*2.54 ± 0.07*	*2.47 ± 0.07*
data finally proposed in [89RIG]	2	$NaClO_4$	4.6 ± 0.3	2.54 ± 0.07	2.47 ± 0.07
this review	2				1.96 ± 0.2
data finally proposed in [89RIG]	3	$NaClO_4$			2.9 ± 0.2

equilibrium and the specific interaction coefficients involved in this reaction

$$\Delta\varepsilon_2 = \varepsilon(NpO_2(CO_3)_2^{3-}, Na^+) - \varepsilon(NpO_2CO_3^-, Na^+) - \varepsilon(CO_3^{2-}, Na^+) \qquad = -0.04 \pm 0.10 \text{ kg/mole.}$$

The $\Delta\varepsilon_2$ and k_2 determinations are very difficult because the $NpO_2(CO_3)_2^{3-}$ is the predominating species in a very narrow chemical domain or even hardly predominates (at high ionic strength). Interference with either the NpO_2^+ species at low carbonate concentration, or the $NpO_2(CO_3)_3^{5-}$ complex at high carbonate concentration, can hardly be avoided. In addition, the $NpO_2(CO_3)_2^{3-}$ pick is at a wavelength between the ones of the NpO_2^+ and of the $NpO_2(CO_3)_2^{3-}$ picks, with also an intermediary molar absorptivity, which do not allow qualitative interpretation (prior to curve fitting or to help its interpretation). For this reason, this review did not use these data. Still, the author pointed out that the above difficulty cancelled when studying ionic strength influence: she used ionic strength shift of the absorbance vs. $\log_{10}[CO_3^{2-}]$ curves to determine the above $\Delta\varepsilon_2$ and $\Delta\varepsilon_3$ values that are indeed in fair agreement with the values determined by this review (from other published data). This review repeated Riglet's graphical determination and found

$$\Delta\varepsilon_3 \quad = \quad -0.08 \pm 0.05 \text{ kg/mole}$$

(there was not enough information to repeat the $\Delta\varepsilon_2$ determination). This confirms that Riglet experimental measurements were reliable and of good accuracy. Still it was not possible to propose and check an accurate interpretation of all the spectrophotometric work for the reasons explained below. For this reason, this review did not use the above estimations of $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ numerical parameters to select thermodynamic data. Riglet also fitted all the results together; but she did not succeed to propose a set of numerical parameters consistent with all here spectrophotometric and solubility (see below) experimental results within the statistical uncertainties (calculated with this curve fitting). She then increased uncertainty, which is perfectly correct. This review followed the author, when she estimated that this inconsistency was due to unknown molar absorptivity coefficients of $NpO_2(CO_3)_2^{3-}$, that had to be fitted. This is classical, and usual statistical analysis does not take into account correctly this uncertainty. This induces large uncertainty on the values of classical formation constants $\beta_2 = k_1 k_2$, and of $\beta_3 = k_1 k_2 k_3$.

This thesis also reported and discussed Np(V) solubility in carbonic / bicarbonate / carbonate aqueous solutions. They are the experimental data, that appeared in several Vitorge's publications [84VIT, 86GRE/ROB], and reports of European joint research contracts [85COM, 85KIM]. Sensitivity analysis was shown in [89RIG page 153]. The thermodynamic data deduced from these works by the author and by this review are consistent within uncertainty (see the table). This review followed the author, when she estimated that the main uncertainty was due to poor crystallisation of the solid phase when NpO_2^+ was the major soluble complex. As mentioned elsewhere in this appendix (see the discussion of

Table VIT1: Determination of the stoichiometry of a hydrated $Na_{2x-1}NpO_2(CO_3)_{x(s)}$ solid phase from Vitorge et al.'s solubility data [84VIT, 85COM, 85KIM, 86GRE/ROB, 89RIG]. x and K_{sx} were calculated by linear regression (see text) on the "data used". Np(V) was first precipitated ("Precipitation 1), then dissolved ("Dissolution 1"), precipitated again ("Precipitation 2") and so on... by varying the pH with $HClO_4$ or $NaHCO_3$ additions in a unique cell were CO_2 was bubbling.

n°	data used	x	$\log_{10}K_{sx}$	$\log_{10}K_{s1}$
1	Precipitation 1	0.53	-8.18	-10.30 ± 0.47
2	Dissolution 1	0.89 ± 0.06	-10.43 ± 0.46	-10.42 ± 0.26
3	Precipitation 2	0.98 ± 0.09	-11.33 ± 0.59	-10.53 ± 0.10
4	Dissolution 2	0.94 ± 0.07	-11.10 ± 0.51	-10.61 ± 0.09
5	Precipitation 3	0.95 ± 0.09	-11.22 ± 0.65	-10.67 ± 0.31
6	3 + 4 + 5	1.04 ± 0.07	-11.78 ± 0.32	-10.63 ± 0.27
7	3 + 4 + 5 + 6	1.02 ± 0.07	-11.60 ± 0.30	-10.57 ± 0.32

Table VIT2: Curve fitting results of Vitorge et al.'s solubility measurements of Np(V) in 2M $NaClO_4$ carbonate / bicarbonate / carbonic aqueous solutions [84VIT, 85COM, 85KIM, 86GRE/ROB, 89RIG]. $\log_{10}K_{sj} = [Na^+]^{2j-1} [NpO_2^+] [CO_3^{2-}]^j$ is $Na_{2j-1}NpO_2(CO_3)_{j(s)}$ solubility product. $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2^+] [CO_3^{2-}]^i)$. All these data were calculated from the same set of experimental measurements, except the two first lines [84VIT] that only used preliminary results. The data proposed by this review used the minimum solubility values to determine K_{s1} and not the best fit obtained by minimising Σ^2 (of K_{s1} and $K_{s1}\ \beta_i$), the least square sum. In the column ±, 1.96 Σ is tabulated as calculated by this review. Uncertainty (calculated by this review) is 1.96 standard deviation on a weighted mean of the corresponding equilibrium constant.

reference	$\log_{10}K_{s1}$	$\log_{10}K_{s1}\ \beta_1$	$\log_{10}K_{s1}\ \beta_2$	$\log_{10}K_{s1}\ \beta_3$	±[b]	$\log_{10}\beta_1$	$\log_{10}\beta_2 / \beta_1$	$\log_{10}\beta_3 / \beta_2$
[84VIT]	-10.92	-6.32	-2.80	-0.48		4.60	3.52	2.32
[84VIT][a]						4.12	4.48	2.16
[85COM]	-10.50	5.90	2.38	-0.06		4.60	3.52	2.32
[86GRE/ROB][b]	-10.56±0.34	-5.47±0.45	-2.41±0.25	-0.10±0.15	0.269	5.09±0.57	3.06±0.21	2.31±0.14
best fit	-10.63±0.38	-5.30±0.32	-2.50±0.75	-0.07±0.15	0.114	5.33±0.51	2.80±0.67	2.43±0.10
this review	-10.65±0.33	-5.40±0.32	-2.50±0.33	-0.01±0.17	0.250	5.25±0.29	2.90±0.17	2.49±0.07

reference	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}K_{s2}$	$\log_{10}K_{s2}\ \beta_3$
[84VIT]	8.12	10.44		
[84VIT][a]	8.60	10.76		
[85COM]	8.12	10.44	-16.40	-6.36
[86GRE/ROB][b]	8.15±0.43	10.46±0.38	-12.44	-1.98
best fit	8.13±0.84	10.56±0.41		
this review	8.15±0.46	10.64±0.37	-12.31±0.87	-1.67±0.79

[a] Assuming the formation of $Na_{0.72}NpO_2(CO_3)_{0.86(s)}$ solid phase. [b] Uncertainty calculated by this review, [85KIM and 89RIG] reported the same numbers as the [86GRE/ROB] publication.

the publication [84VIT] in this appendix), this relatively poor accuracy could hardly be attributed to ionic exchange equilibria in the solid phase:

$$2\ (x-1)\ Na^+ + NaNpO_2CO_{3(s)} \Leftrightarrow Na_{2x-1}NpO_2(CO_3)_{x(s)} + (1-x)\ CO_3^{-2}$$

because Volkov proposed such reactions (but usually not equilibrated with aqueous solutions), typically the formation of hydrated $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$ [79VOL/VIS]. Vitorge tested this interpretation of the preliminary solubility measurements [84VIT], in the chemical conditions where NpO_2^+ was the major soluble complex he assumed that the

$$Na_{2x-1}NpO_2(CO_3)_{x(s)} \Leftrightarrow (2\ x - 1)\ Na^+ + NpO_2^+ + (1-x)\ CO_3^{-2}$$

equilibrium controlled the solubility and deduced the corresponding solubility product, K_{sx}, and x values from linear regression since $\log_{10}[Np(V)]$ vs. $\log_{10}[CO_3^{-2}]$ plot was a straight line with slope about -1. He found the $Na_{0.72}NpO_2(CO_3)_{0.86(s)}$ stoichiometry; but the accuracy was not enough to reject possible formation of hydrated $NaNpO_2CO_{3(s)}$. This review followed this treatment of the data for each series of dissolution or precipitation of Np(V). It was found that the linear regression results were more accurate for dissolution than for precipitation, with time the x value became closer to 1 and the K_{s1} decreased (see the table). This is an evidence that hydrated $Na_{2x-1}NpO_2(CO_3)_{x(s)}$ with $x < 1$ was certainly formed initially; but that this solid phase was metastable, and was slowly transformed to a thermodynamic stable one, hydrated $NaNpO_2CO_{3(s)}$. This is consistent with the X-ray diffraction results and with the series of observations by Volkov et al. (see the discussion of the publication [84VIT] in this appendix); but $Na_{2x-1}NpO_2(CO_3)_{x(s)}$ hydrated solid phases proposed by Volkov et al. are probably metastable when equilibrated with aqueous solutions. They are then not credited by this review. Note that if a $Na_{2x-1}NpO_2(CO_3)_{x(s)}$ solid phase with $x < 1$ is formed, it would be transformed into the $NaNpO_2CO_{3(s)}$ one when increasing the free carbonate concentration, one would then expects a correlation between the error ($[Np]_{measured} - [Np]_{calculated}$) and $[CO_3^{-2}]$ which was not detected by this review. This confirmed that the scattering of the data was due to kinetic problem. This means than the influence of the ionic exchanged equilibrium in the solid phase, if any, was less important than the kinetic problem. Finally, the scattering of the data was rather due to slow crystallisation and possible variation of the number of water molecules in the hydrated solid compounds as discussed in the [93LEM/BOY] publication. Depending on chemical conditions, solubility was controlled by the

$$NaNpO_2CO_{3(s)} + (i - 1)\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_i^{1-2i} + Na^+$$

equilibria, and the corresponding equilibrium constants, $K_{s1,i} = K_{s1}\ \beta_i$, are directly determined from this type of measurements. So they each include the K_{s1} solubility product whose numerical value depends on the above problems in the solid phase. To minimise this possible systematic error due to the solid phase, this review used instead the stepwise formation constants $k_i = \beta_i / \beta_{i-1}$. This also allowed comparison with equilibrium constants measured by other techniques. There is only one later work [91KIM/KLE, 94NEC/KIM, 94NEC/RUN and 95NEC/RUN] by Kim's group of Np(V) carbonate complexes at the same ionic strength; but comparison is not very useful because this later work (see its discussion in this appendix) had problems with the calibration of $[CO_3^{-2}]$ determination (from pH measurements). Vitorge's group complexing constants at I = 3 M [84VIT, 85COM, 85 KIM and 86GRE/ROB] are in fair agreement with other reliable data at lower ionic strength and with the above [89RIG] spectrophotometric results. This review then used these data to extrapolate the complexing constant to zero ionic strength. The $NaNpO_2CO_{3(s)}$ solubility product measured here [89RIG and 86GRE/ROB] is lower than the ones measured at room temperature by Maya [83MAY] or by Kim's group, while it is a little more than Lemire's determination at 30°C [93LEM/BOY]. The maximum difference between all these values was about 1 $\log_{10}$ unit. Following Lemire, this review attributed this difference to change in the solid phase: at 30°C there are indications that the solid phase should be less hydrated than at lower temperature, the exact temperature for this phase transition is not known. It seems that the time for preparing the solid compound was longer in the [89RIG and 86GRE/ROB], and that its X-ray diffraction pattern was possibly different (as discussed in this appendix for the [91KIM/KLE and 93LEM/BOY] publications). All this indicates that there are possibly at least two hydrated $NaNpO_2CO_{3(s)}$ solid phases, and that they were not the same ones in all the above publication. For this reason no linear regression to zero ionic strength was finally used to propose a unique equilibrium constant involving $NaNpO_2CO_{3(s)}$ solid (typically its solubility product).

At higher carbonate concentration where batch experiments were used, 4 weeks were needed to achieve equilibrium, while 2 weeks were not really enough. This indicates that probably all the other published data on hydrated $NaNpO_2CO_{3(s)}$ at room temperature were slightly out of equilibrium; but this kinetic problem was usually not mentioned. In 0.1 M carbonate (I = 3 M $NaClO_4$) solution, the expected solubility was higher than the measured one. This was an evidence of the formation of a new solid phase. The authors identified a hydrated $Na_3NpO_2(CO_3)_{2(s)}$ solid phase by its X-ray diffraction pattern. The same observation was also made for some of the data in 0.025 M CO_3^{-2} aqueous solution. Some of these data are the same (within uncertainty) that those previously measured by Simakin who used a hydrated $Na_3NpO_2(CO_3)_{2(s)}$ solid phase as starting material and proposed the following equilibrium

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ Na^+$$

This review followed Simakin's interpretation (see the discussion on the [77SIM] publication in this appendix: $\log_{10}K_{s2,3} = -1.46 \pm 0.09$ was calculated by this review from Simakin's data). Still, some of the data in 0.1 M CO_3^{-2} solution reported in [89RIG] are lower ($\log_{10}K_{s2,3}$ = -1.37 to -1.97 was evaluated by this review then $\log_{10}K_{s2,3} = -1.67 \pm 0.30$ was deduced). A new solid phase was then again precipitating slowly. This could be a better crystallised $Na_3NpO_2(CO_3)_{2(s)}$ hydrated compound, that also possibly was hydrated in a different way. This could also be a Na-Np(V)-CO_3 hydrated compound with CO_3 / Np(V) more than 2.

[90NIT/STA]

Nitsche H., Standifer E., Silva R. *Neptunium(V) complexation with carbonate.* Lanthanide Actinides Res. 3, 203-211 (1990).

Nitsche, Standifer and Silva measured the formation constant of the first Np(V) carbonate complex by absorption spectrophotometry, in 0.1 M $NaClO_4$ aqueous solution. Their results are in accord with the previous Riglet's similar work [89RIG]. They used the SIT to extrapolated their data to zero ionic strength, with other published data. They discuss these data in quite a similar way than the first draft of the present review; but they did not use the data in 3 M $NaClO_4$ medium [86GRE/ROB and 89RIG]. The β_1 value proposed in this publication [90NIT/SIL] correspond exactly to the SIT prediction shown on the figure 3 of the publication. Their results are consistent with those selected by this review; but there are small problems with this work.

First the authors did not give the exact composition of their solution which do not allow recalculation by this review, typically to check the correction that they used for Np(V) hydrolysis that they overestimated. They calculated from published data that 28 % of hydrolysis species were present in their solutions. Since they observed an isobestic point, they had to assume that this Np(V)-OH species had the same molar absorptivity coefficient as the NpO_2^+ species. This assumption was not verified. Even if it is the most reasonable one (if no spectral change due to hydrolysis) it is not the only possible one (the hydrolysis and carbonate Np(V) species could also have the same spectrum) and it is quite unusual to observe actinide hydrolysis without spectral change. Anyhow, following the hydrolysis constant selected by this review, this correction should be less than the uncertainty. This review then calculated that neglecting this correction lead to

$\log_{10}\beta_1 = 4.22$ instead of

$\log_{10}\beta_1 = 4.34 \pm 0.11$ in 0.1 M $NaClO_4$ proposed in [90NIT/STA]

Second they calibrated their glass electrode with standard buffer and they used a 4 M NaCl solution as a bridge electrolyte: it is not clear whether this could avoid junction potential.

Third they used a linear regression to check the stoichiometry and to calculate the formation constant of the equilibrium under study. They found a slope 0.94 ± 0.04 (increasing the uncertainty to 1.96 σ) which is not consistent with the theoretical value of 1. Even if one admit that this uncertainty is underestimated (typically because their was not enough independent measurements), the formation constant calculated was

$$\frac{[Np(V)]}{[NpO_2^+][CO_3^{-2}]^{0.94}}\ (mol./l)^{-0.94} \quad \text{and not } \beta_1 = \frac{[Np(V)]}{[NpO_2^+][CO_3^{-2}]}\ (mol./l)^{-1}$$

the authors should instead have calculated the mean value of $\log_{10}\beta_1$ (to be consistent with the mass action law).

Table [90NIT/STA]: Curve fitting results of the first Np(V) carbonate complexation, from the spectrophotometric measurements reported in the [90NIT/STA] publication in 0.1 M $NaClO_4$ aqueous solutions. A_0 and A_1 are NpO_2^+ and $NpO_2CO_3^-$ molar absorptivity respectively. $\pm_A$ and $\pm_{log10A}$ are 1.96 standard deviations on A and $log_{10}A$ respectively where A is the measured molar absorbance. When $log_{10}\beta_1$ is not fitted, it is the weighted mean value calculated from each experimental measurement.

	Fitted parameters	$\pm_A$	$\pm_{log10A}$	A_0	A_1	$log_{10}\beta_1$		
	A_1, $log_{10}\beta_1$	21.88	0.051	395	49.8	4.73	±	0.17
	A_1	22.78	0.052	395	47.2	4.74	±	0.17
	A_1, $log_{10}\beta_1$	23.90	0.042	395	36.7	4.66	±	0.17
	A_1	23.06	0.050	395	41.7	4.71	±	0.17
	A_1, A_0, $log_{10}\beta_1$	9.81	0.028	353	25.8	4.51	±	0.06
	A_1, A_0	9.81	0.028	352	25.8	4.51	±	0.06
	A_1, A_0, $log_{10}\beta_1$	9.83	0.028	351	24.7	4.51	±	0.06
	A_1, A_0	9.83	0.028	352	24.7	4.51	±	0.06
[90NIT/STA] corrected for Np(V)-OH	A_1			?		4.34	±	0.11
[90NIT/STA] no corrections (this review)	A_1			?		4.46	±	0.23
[90NIT/STA] proposed by this review						**4.56**	**±**	**0.67**

It is not clear whether this publication used absorbency, or the area under picks (in the latter case it does not seem to be correct).

Possibly each of these small systematic errors could be neglected. Possibly they could not, but they cancelled. Anyhow there are not enough information in this publication to evaluate these possible errors.

This review scanned the spectrophotometric results from the figure 1 of this publication and used the $log_{10}[CO_3^{-2}]$ given in its table 1, to perform curve fitting (see the table). The results are not consistent with the NpO_2^+ molar absorptivity coefficient, A_0, used in this publication, so it was also fitted by this review. The value

$log_{10}\beta_1$ = 4.34 ± 0.11 proposed in [90NIT/STA] are consistent with
$log_{10}\beta_1$ = 4.51 ± 0.06 best value
$log_{10}\beta_1$ = 4.74 ± 0.17 where the A_0 was not fitted.

This confirms that there is some systematic error. This review calculated that the formation of the $NpO_2(CO_3)_2^{-3}$ complex had negligible effect. Then this review increased the uncertainty to overlap all the fitting results and doubled it (see the table).

[90RIG]

CEA-R-5535, 1990, in French. This CEA report is the [89RIG] thesis.

[91KIM/KLE]

Kim J.I., Klenze R., Neck V., Sekine T., Kanellakopulos B. *Hydrolyse, Carbonat- und Humat- Kompleixierung von Np(V).* RCM 01091. Institut für Radiochemie der Technischen Universität München July (1991).

The work presented in this report has been published later [94NEC/RUN], and were used in a series of publications of this laboratory [94MEI, 94NECK/KIM, 95FAN/NEC, 95NEC/FAN and 95NEC/RUN], that proposed equilibrium constants and activity coefficients for Np(V) in OH^- / CO_3^{-2} / HCO_3^- / CO_2 aqueous solutions at 25°C. Older work by this laboratory had to be corrected [95SIL/BID page 281] for liquid junction effects on the calibration of their glass electrode. Another methodology was used here for pH calibration; but this review still found some problems with it (see below). Kim at al. measured Np(V) solubility in aqueous solutions of constant ionic strength: 0.1, 1 and 3 M $NaClO_4$. It is the same type of measurements previously reported by Vitorge et al. [84VIT, 85KIM, 85COM, 86GRE/ROB and 89RIG], whose publications and reports were summarised by Kim for European reports [85KIM and 85COM]. The values of the solubility product and complexing constants measured in this report [9IKIM/KLE], are the same as those reported in the publication [94NEC/KIM]. The results of solubility measurements were tabulated in the [9IKIM/KLE] report. Extra measurements in 5 M $NaClO_4$ media were tabulated in the [94NEC/KIM] report. In this [91KIM/KLE p30 to 33] report $NaNpO_2CO_{3(s)}$ was transformed slowly into the $Na_3NpO_2(CO_3)_{2(s)}$ in 1 and 3 M Na^+ media as already found [86GRE/ROB]. This transformation occurred after 10 days. This type of solid transformation and other ones could decrease the accuracy of solubility measurements as discussed in this appendix in several places from the work of Vitorge [84VIT, 85KIM, 85COM and 86GRE/ROB] or of Lemire [93LEM/BOY]. For this reason, it could be found quite surprising that evidence of solid phase transformation was reported and discussed in Kim's work [91KIM/KLE]; but no scattering of the data was reported. Careful examination of the original solubility data indicated scattering of the data in the $NpO_2CO_3^-$ predominance domain, smaller than reported by Vitorge [84VIT] and Lemire [93LEM/BOY], while no scattering at all was reported in the chemical conditions used to determine the solubility product, K_{s1}, and the second complexing constant, β_2. This point was not much discussed by Kim et al. A minimum time (3 weeks) was needed to prepare the $NaNpO_2CO_{3(s)}$ hydrated solid phase at (possibly metastable) equilibrium; a few more days [84VIT, 89RIG and 94NEC/RUN] are enough to reach equilibrium condition in the dissolution direction; while after a few more days (depending on the chemical conditions) the solid start to be slowly transformed into a $Na_3NpO_2(CO_3)_{2(s)}$ hydrate.

Even if Kim et al. used the detailed experimental information that they had from Vitorge's work, to choose the exact time needed for equilibration, it is surprising that they did not get more points out of equilibrium, at least because they did not use exactly the same equilibration procedure. So they possibly eliminated outliers, or the experimental data presented are already the result of a statistical treatment.

Table [94NEC/RUN]: Junction potential of Kim et al.'s measurements in 0.1 to 5 M $NaClO_4$ aqueous solutions. M is [$NaClO_4$]. X activity coefficient is γ_X mol.kg^{-1} and y_X mol.l^{-1}. $\gamma'_{OH^-} = \gamma_{OH^-} / a_{H2O}$ mol.kg^{-1}, $y'_{OH^-} = y_{OH^-} / A_{H2O}$ mol.l^{-1}, where a_{H2O} or A_{H2O} is the activity of water in molal and molar units. ΔpH is the pH correction reported in [94NEC/RUN] for calibration of the glass electrode in acidic (left side of the table) and basic (right side) aqueous solution. ΔpH probably included activity coefficients and junction potential. This review then calculated the activity coefficient theoretical effects in both media, $-\log_{10}y_{H^+}$ and $-\log_{10}\gamma'_{OH^-}$ respectively, and attributed the remaining correction, pE_j to junction potential effect. K_{p2} is the value of the $[CO_3^{-2}]\ [H^+]^2 / P_{CO2}$ equilibrium constant calculated by this review. K'_{p2} is its value measured in the [94NEC/RUN] publication. The shift is $\log_{10}K'_{p2} - \log_{10}K_{p2}$.

mol.l^{-1} M	molal $-\log_{10}\gamma_{H^+}$	molar $\log_{10}y_{H^+}$	molar ΔpH	molar pE_j	molal $\log_{10}\gamma'_{OH^-}$	molar $\log_{10}y'_{OH^-}$	molar? ΔpH	molar? pE_j	molar $\log_{10}K'_{p2}$	molar	molar shift
0.1	0,10	0,10	0.02	-0.08	-0,10	-0,10	0.01	0.11	-17.56±0.09	-17.53±0.04	-0.03±0.10
1	0,06	0,08	0.35	0.27	-0,15	-0,15	0.33	0.48	-17.47±0.10	-17.51±0.07	-0.26±0.12
3	-0,24	-0,17	0.64	0.81	-0,05	-0,05	0.64	0.69	-17.99±0.12	-17.61±18	-0.38±0.22
5	-0,65	-0,53	0.90	1.43	0.10	0.10	0.86	0.76			

This series of Kim's et al. publications is the first attempt by this laboratory, to use ionic strength corrections and to take into account liquid-liquid junction; but there are still some problems in the [94NEC/RUN] publication. They used a wrong definition of the pH involving the mean activity coefficient of $HClO_4$ (instead of the H^+ activity coefficient in $NaClO_4$ aqueous solutions). This could be an approximation, but when using the SIT (as they did) the $\varepsilon(H^+,ClO_4^-)$ and $\varepsilon(Na^+,ClO_4^-)$ values are not the same. This type of approximation is anyhow no more valid when using third virial expansion as they did later [95NEC/RUN]. It is also not clear which molality to molarity conversion factor they used. Their calibration procedure might still have been self consistent since this review checked that they measured values of the water ionic product, in accord with published data, and with the SIT as used by this review. On the other hand it was not the case for their values of the carbonic acidic constants. They did not discuss this point. It might be attributed to their experimental methodology for controlling carbonate speciation; but this would not explain why the error increased with ionic strength. They fond a deviation of 0.03 to 0.38 $\log_{10}$ unit (see the table). This review then increased the uncertainty for this systematic error (column shift in the table) in $\log_{10}[CO_3^{-2}]$ determination. This review estimated the junction potential (table) from the information given in the [94NEC/RUN] publication: this correction was quite important. There is no way to predict it since it strongly depends on the experimental set up. Junction potential estimated in acidic media increases almost linearly with concentration up to about 80 mV, which seems reasonable.

Different results were found in basic media which is not consistent. 3 M NaCl liquid junction was used, so the junction potential correction is expected to be minimum at about I = 3M which was not the case. The author then probably made other corrections that they did not report, and the explanation given for this calibration was not completely understood by this review. Anyhow the authors did not actually use classical notations to allow correct comparison with thermodynamic standard. Finally some of their calibration was correct, others were not. It was not possible to decide whether they were due to chemical reason (carbonate equilibration), incorrect junction potential correction or methodological error (wrong pH definition). Most of these problems were the same during solubility measurements and they certainly cancelled. For this reason, this review used the value at zero ionic strength.

To recalculate the stability constants proposed by Kim's group, this review used the experimental solubility measurements tabulated in the [91KIM/KLE and 94NEC/RUN] reports and scanned those in 5 M NaCl aqueous solution of the figure 3d of the [95NEC/RUN] publication. It was probably the characterisation of the initial solid and not the study of the solid compound after sampling for solubility measurements. The authors claimed that they had no problem with the solid phase and published X-ray diffraction patterns [95NEC/RUN]. This is then in contradiction with Vitorge and Lemire observations; but this point is not much discussed in Kim's publications. It was claimed [95NEC/RUN] that the same solid compounds were obtained by Maya and by Grenthe, Robouch and Vitorge which is in contradiction with what the last authors said and with their X-ray analysis. This review then considered that there was possibly in this solubility work, the same problem with the solid phase as already discussed in this appendix for the [84VIT, 86GRE/ROB, 89RIG and 93LEM/BOY] publications, and analysed the solubility data as for the [89RIG] publication.

Anyhow, as explained above there was also a problem with the calibration of the $[CO_3^{-2}]$ determination, that cancelled at I = 0. This review then used only the set of Kim's group solubility measurement at I = 0 to select thermodynamic data. This review also found that Kim's group ionic strength corrections were not consistent for solubility products, for which well known independent parameters were used to estimate the corresponding ionic strength corrections (see the discussion of the [94NEC/RUN] publication in this appendix); they were neither consistent with a later publication [95FAN/NEC] of this group.

Finally the solubility product for the hydrated $NaNpO_2CO_{3(s)}$ measured by Kim's group and extrapolated to zero ionic strength by this review, was slightly bigger than in the reliable solubility studies [83MAY, 86GRE/ROB and 93LEM/BOY] considered by this review. It might then correspond to a freshly precipitated one. His solubility data in 1 M $NaClO_4$ aqueous solutions were exactly the same as Maya's one which is bit surprising because both works did not use the same acidic equilibrium constant for the carbonic acid when calibrating their glass electrode. In 3 M $NaClO_4$ aqueous solutions Kim's group solubility results are clearly different from those of the [86GRE/ROB] previous publication. Possible shift in pH calibration (as explained above) was not enough to explain the discrepancy that should be due to the solid phases that were different in the two studies. The main consequence of this discrepancy between experimental results at I = 3M, is reflected on the value of the first complexing constant, β_1, which would have a dramatic effect on its extrapolation to zero ionic strength (then on the value of $\varepsilon(NpO_2CO_3^-, Na^+)$) and on the accuracy of $\beta_1°$. The stepwise constants, k_2 and k_3, are in agreement with the values selected by this review, even up to I = 5 M. This was unexpected: the SIT approximation is usually not valid at such high ionic strength and there was a possible systematic deviation at high ionic strength. Possibly all these errors cancelled. In conclusion, as for other published solubility works, this review made a separate discussion and

Table KIM1: Curve fitting results on Kim et al.'s solubility measurements of Np(V) in carbonate / bicarbonate / carbonic aqueous solutions [91KIM/KLE, 94NECK/KIM, 95FAN/NEC, 95NEC/FAN and 95NEC/RUN]. $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2^+]\ [CO_3^{2-}]^i)$. $K_{sj} = [Na^+]^{2j-1}\ [NpO_2^+]\ [CO_3^{2-}]^j$ is hydrated $Na_{2j-1}NpO_2(CO_3)_{j(s)}$ solubility product. $K_{ss} = K_{s2} / K_{s1}$. The best fit[b] was obtained by minimising Σ^2 (of K_{s1} and $K_{s1}\ \beta_i$), the least square sum. In the column ±, $1.96\ \Sigma/\sqrt{n}$ was calculated by this review, where n is the number of measurements. Uncertainty (calculated by this review) is 1.96 standard deviation on a weighted mean of the corresponding equilibrium constant, it was not increased for systematic error (see text) in this table to allow statistical comparison. The values[e] proposed by this review (from Kim et al.'s experimental data or from all published experimental data in the same media) are bolded. T = 25°C. $NaClO_4$ media except the last line at I = 5 M (NaCl).

	I (M)	$\log_{10}K_{s1}$	$\log_{10}K_{s1}\ \beta_1$	$\log_{10}K_{s1}\ \beta_2$	$\log_{10}K_{s1}\ \beta_3$	±[b]	$\log_{10}\beta_1$	$\log_{10}\beta_2 / \beta_1$	$\log_{10}\beta_3 / \beta_2$
(a)	0.1	-10,28±0.04	-5,70	-3,68	-3.58[c]	0.110	4,58±0.04	2,02	0.10[c]
(a,d)	0.1	-10,29±0,22	-5,70±0,21	-3,70±0,34	-3.59[c]	0,109	4,59±0,30	2.00±0,23	0.11[c]
(a,e)	**0.1**	**-10,29±0,13**	**-5,78±0,20**	**-3,70±0,36**	-3,59[c]	0,146	**4,51±0,19**	**2,08±0,19**	0,11[c]
(a)	1	-10,10±0.03	-5,60	-3,14	-1,43	0,048	4,50±0.04	2,46	1,71
(a,d)	1	-10,10±0,10	-5,58±0,10	-3,13±0,13	-1,42±0,10	0,042	4,52±0,10	2,45±0,10	1,71±0,10
(a,e)	1	**-10,10±0,10**	**-5,62±0,10**	**-3,13±0,10**	**-1,42±0,10**	0,056	**4,48±0,10**	**2,49±0,10**	**1,71±0,10**
(b)	1	-10.14±0.04	-5.65	-3.03	-1,61	0,104	4,49±0,06	2,62	1,42
(b,e)	1	-10.12±0.35	-5.55±0.35	-3.10±0.24	-1,60±0,41	0,097	4,57±0,35	2,45±0,26	1,50±0,36
(a,b,d)	1	-10.11±0.09	-5.57±0.11	-3.13±0.36	-1,46±0,25	0,082	4,54±0,14	2,44±0,15	1,67±0,10
(a,b,e)	**1**	**-10.10±0.10**	**-5.61±0.11**	**-3.15±0.31**	**-1,44±0,24**	0,096	**4,49±0,15**	**2,46±0,10**	**1,71±0,10**
(a)	3	-10.45±0.04	-5.69	-2.76	-0.15	0.444	4.76±0.04	2.93	2.61
(a,d)	3	-10.45±0.10	-5.69±0.10	-2.76±0.10	-0.16±0.10	0.444	4.77±0.10	2.93±0.10	2.60±0.10
(c,e)	3	-10.65±0.33	-5.40±0.34	-2.50±0.33	-0.01±0.17	0.250	5.25±0.29	2.90±0.17	2.49±0.10
(a,c,d)	3	-10.65±0.51	-5.75±0.76	-2.35±0.14	-0.05±0.21	0.437	4.9 ±0.9	3.4 ±0.4	2.30±0.17
(a)	5	-11.06	-6.06	-2.77	0.41	0.185	5.00	3.29	3.18
(a,d)	5	-11.07±0.14	-6.02±0.17	-3.29±0.34	0.55±0.14	0.142	5.04±0.22	2.73±0.24	3.84±0.80
(a,e)	**5**	**-11.07±0.18**	**-6.15±0.18**	**-2.75±0.29**	**0.45±0.27**	**0.177**	**4.92±0.25**	**3.40±0.14**	**3.20±0.24**
(g)	5	-10.63±0.11							
(h)	5				0.14±0.15				

	I (M)	$lob_{10}\beta_2$	$lob_{10}\beta_3$	$lob_{10}K_{s2}$	$lob_{10}K_{s2}\ \beta_3$	$lob_{10}K_{ss}$
(a)	0.1	6,60±0.07	6.70[f]			
(a,d)	0.1	6,59±0.40	6.70[f]			
(a,e)	**0.1**	**6,59±0.38**	6.70[f]			
(a)	1	6,96±0.06	8,67±0.09	-12.23[g]±0.15	-3.56[g]±0.17	-2.13±0.17
(a,d)	1	6.97±0.13	8.68±0.10			
(a,e)	**1**	**6.97±0.10**	**8.68±0.10**	**-12.25±0.33**	**-3.57±0.30**	**-2.15±0.32**
(b)	1	7.11±0.07	8.53±0.09			
(b,e)	1	7.03±0.24	8.52±0.41			
(a,b,d)	1	6.98±0.37	8.65±0.27			
(a,b,e)	**1**	**6.95±0.32**	**8.66±0.26**			
(a)	3	7.69±0.07	10.30±0.09	-12.59±0.10	-2.29±0.15	-2.14±0.15
(a,d)	3	7.70±0.11	10.29±0.10			
(c,e)	3	8.15±0.46	10.64±0.37	-12.31±0.48	-1.67±0.30	-2.11±0.37
(a,c,d)	3	8.3 ±0.5	10.6 ±0.55			
(a)	5	8.29	11.47	-13.57±0.11	-2.10±0.14	-2.51±0.15
(a,d)	5	7.77±0.23	11.62±0.21			
(a,e)	**5**	**8.32±0.34**	**11.52±0.32**			
(g)	5			-12.48±0.23		-1.85±0.25
(h)	5				-1.50±0.3	-1.64±0.34

[a] [91KIM/KLE, 94NEC/KIM]. [b] [83MAY]. [c] [86GRE/ROB]. [d] Best fit calculated by this review. [e] Minimum solubility (and not mean or fitted values) assuming that scattering of the data was due to solid transformation (see text and the discussion of the [86GRE/ROB] publication. [f] A β_3 fixed value was added by this review. [f] A $K_s\ \beta_1$ fixed value was added by this review. [g] [95NEC/RUN] 5M NaCl. [h] Graphically estimated by this review from the figure 3d of the [95NEC/RUN] publication and using the same correction as in the [95NEC/RUN] publication for chloride complexation.

treatment for solubility product problem. Then only the first complexing constant at high ionic strength deviate by more than 0.3 $\log_{10}$ unit from other published works as reinterpreted by this review. The origin of this deviation was not understood.

Spectra of Np(V) carbonate complexes were also reported [91KIM/KLE]. They are in accord with those previously found by Riglet [89RIG]. They were used later [94NEC/RUN] to calculate the formation constants of two Np(V) carbonate complexes. The first complexing constant, β_1, value measured by spectrophotometry is not consistent (within the uncertainty estimated by the authors) with its value measured by solubility technique. The same observation stands for the β_2 values reported in [94NEC/RUN]. This inconsistency was pointed out by the authors; but it was not explained. This review noticed that the values of the stepwise constant, $k_2 = \beta_2/\beta_1$, measured by each technique, are the same ones. This review attributed this inconsistency to the evaluation of the uncertainty by the authors (who are too optimistic in evaluating their experimental accuracy) and to systematic error in solubility measurements due to poor crystallisation of the solid phase in critical chemical conditions for the determination of the β_1 value, as discussed above and by Vitorge [84VIT, 89RIG] and Lemire [93LEM/BOY].

[91VIT/OLI]

P. Vitorge, J. Oliver, J.P Mangin, A. Billon. *The Study of Physical and Chemical Properties which Affect Migration of Transuranic Elements in the Near Field.* in Task 3, Characterisation of radioactive waste forms. A series of final reports (1985-89) N°30, Luxembourg OOPEC. Contrat FI1W/0035. Final report. EUR 13673 (1991).

This report includes an English translation of a part of Riglet's thesis (see the discussion of [89RIG] in this appendix).

[93LEM/BOY]

Lemire, R.J., Boyer, G.D., Campbell, A.B. *The solubilities of sodium and potassium dioxoneptunium(V) carbonate hydrates at 30, 50 and 75 C*, Radiochim. Acta, 61 (1993) 57-63.

Lemire, Boyer and Campbell studied $NaNpO_2CO_{3(s)}$ and $Na_3NpO_2(CO_3)_{2(s)}$ equilibration with HCO_3^-/CO_3^{-2}, 1 M Na^+ ($NaClO_4$) solutions at 30, 50, and 75°C, and with 0.5 M Na^+ aqueous solutions at 75°C, and $KNpO_2CO_{3(s)}$ equilibration at 30 and 75°C. Most of the results were presented at the Migration'87 conference; but were not published then. The glass electrode was calibrated in concentration ($-\log_{10}[H^+]$) and not activity (pH) units at each temperature. $-\log_{10}[H^+]$) measurements at different temperatures were used to calculate $[CO_3^{2-}]$. Uncertainties mainly came from solid phase transformations and lack of buffering effect at low $[CO_3^{2-}]$. Previous works [74VIS/VOL, 77SIM, 77VOL/VIS, 79VOL/VIS, 81VOL/VIS 83MAY, and 84VIT] on Np(V) solubility and soluble complexes [85BID/TAN, 85INO/TOC] in carbonate media were well documented and used to run and interpret correctly the experiments. Assuming that the

$$NaNpO_2CO_{3(s)} + (i\text{-}1)\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_i^{1-2i} + Na^+,$$

or the

$$Na_3NpO_2(CO_3)_{2(s)} + (i\text{-}2)\ CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_i^{1-2i} + 3\ Na^+$$

equilibrium controlled the solubility. As discussed elsewhere in this appendix [89RIG], hydrated $NaNpO_2CO_{3(s)}$ is not very well crystallised at low $[CO_3^{2-}]$ and temperature. Its solubility was not very much reproducible even during the 2-4 weeks of equilibration time used in this publication [93LEM/BOY]. Previous work [86GRE/ROB] predicted that hydrated $NaNpO_2CO_{3(s)}$ compound is into $Na_3NpO_2CO_{3(s)}$ one, when $[CO_3^{2-}]$ becomes higher than 1 mM in $[Na^+]$=3 M solution (then 9 and 18 mM in $[Na^+]$ = 1 and 0.5 M solutions respectively) It was confirmed by later works [91KIM/KLE, 95NEC/RUN]. The kinetic of this transformation was very slow at 25°C and was found here to be quicker at higher temperature. It was difficult to deduce solubility products and formation constants from curve fitting, because $NpO_2CO_3^-$ was transformed to $NpO_2(CO_3)_2^{3-}$ in the $[CO_3^{2-}]$ domain where a solid phase transformation occurs: this could lead to instability in the fitting algorithm.

To estimate equilibrium constants, this review accepted the qualitative interpretation of this publication [93LEM/BOY] and used a classical graphical procedure, that is described now. The results are in the table. The same notations as in the table are used. At 30°C Lemire et al. found about the same solubility as Maya at 25°C for $[CO_3^{-2}] <$ 1mM, $K_{s1}\ \beta_i$ was them estimated graphically for i = 0, 1 and 2, assuming that some of the data shown of the figure 1a of the publication [93LEM/BOY] corresponded to over saturated solutions. For this reason, the values estimated by this review were smaller than the curve fitting results. At higher carbonate concentration, the initial $NaNpO_2CO_{3(s)}$ solid phase was slowly transformed into a thermodynamically more stable one. This explains the observation on the X-ray diffraction patterns. No thermodynamic data were estimated from those results. The Np(V) solubility using a $Na_3NpO_2(CO_3)_{2(s)}$ solid phase as starting material was in accord with these observations (figure 1b of the publication [93LEM/BOY]) and allowed graphical estimation of $K_{s2}\ \beta_i$ for i = 2 and 3. This is enough to generate all the other equilibrium constants (see the table). There are still some solubility measurements that could not be explained by the above interpretation. Some of them (at 0.2 to 10 mM $[CO_3^{-2}]$) could be an evidence that the final $Na_3NpO_2(CO_3)_{2(s)}$ phase was not really controlling the solubility at the beginning of the experiment, one possible explanation (change in the number of water molecules in the solid phase) were proposed by Lemire et al.. There is still one outlier solubility measurement (at about 0.15 M $[CO_3^{-2}]$).

The same solid phase transformation can explain the solubility measurements at 50 °C (figure 2 of the publication [93LEM/BOY]) $K_{s1}\ \beta_i$ were them estimated graphically for i = 0 and 1, and $K_{s2}\ \beta_i$ for i = 1, 2 and 3 were them estimated graphically in the same way. Rather than taking mean values (as produced by curve fitting) for the equilibrium constant, this review used the minimum solubility for the chemical conditions where solid phase transformation was suspected. As at 30 °C, this interpretation can be valid only if it is assumed that the initial $Na_3NpO_2(CO_3)_{2(s)}$ solid phase was initially not at equilibrium with the aqueous solution (as at 30° C, its number of water molecules might have been changing, or a few per cent of a more soluble phase might have been mixed with it).

The same interpretation was performed by this review from the solubility measurements at 75 °C (figure 3 of the publication [93LEM/BOY]) in 0.5 and 1 M sodium aqueous solutions. There were 5 solubility measurements in K^+ aqueous solutions. One possible interpretation indicates that $K_{s1}\ \beta_1$ is smaller by about 1.4 unit $\log_{10}$ than in sodium medium. Much smaller difference was found between the values of the $K_{s2}\ \beta_3$ constants in both media. Since ionic strength effect should nearly cancel between the two media, this would indicate that the $KNpO_2CO_{3(s)}$ solid phase is more stable than the $NaNpO_2CO_{3(s)}$ one, while the $K_3NpO_2(CO_3)_{2(s)}$ solid phase would be about as stable as the $Na_3NpO_2(CO_3)_{2(s)}$ one.

Solid phase transformation lowered solubility while complexing increased it, resulting in practical constant Np(V) solubility in a wide range of carbonate concentration. Classical curve fitting cannot distinguish between these two effects that resulted in flat solubility curves. This review then used the same type of qualitative interpretation on solid phase evolution than Lemire's: not only the hydrated $NaNpO_2CO_{3(s)}$ and $Na_3NpO_2(CO_3)_{2(s)}$ solid phases control Np(V) solubility. The other solid phases were possibly a partially dehydrated one with the same stoichiometry and another one with intermediary stoichiometry ($Na_{2x-1}NpO_2(CO_3)_{x(s)}$ where 1 < x < 2). Dehydration (if any) was observed between 22-

Table [93LEM/BOY]1: Estimation of formation constants for Np(V) carbonate complexes from solubility measurements of the publication [93LEM/BOY]. ref. are: [1][83MAY] data re-evaluated in the [93LEM/BOY] publication, [2][83MAY] data re-evaluated by this review, [3][93LEM/BOY], [4][93LEM/BOY] data re-evaluated by this review, [5]calculated by this review from some of the formation constants proposed in the [93LEM/BOY] publication, [6]as [4] in 0.5 M Na^+ media, [7]as [4] in 1 M K^+ media. The data are in 1 M Na^+ media, except [6] and [7]. $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2^+] [CO_3^{-2}]^i)$, $K_{sj} = [Na^+]^{1-2j} [NpO_2^+] [CO_3^{-2}]^j$ is the solubility product of a $Na_{1-2j}NpO_2(CO_3)_j$ hydrated solid phase. For each ref., a minimum needed set of data was calculated by curve fitting [93LEM/BOY] or graphically (this review), the other ones were calculated from them. Two K_{s2} values were proposed at 30°C, because at this temperature, the $NaNpO_2CO_{3(s)}$ hydrated solid phase is assumed to be transformed into a less hydrated one.

ref.	°C	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}k_2$	$\log_{10}k_3$	$\log_{10}K_{s1}$	$\log_{10}K_{s1}\ \beta_1$
1	25	4.6 ± 0.1	7.1 ± 0.1	8.5 ± 0.1	2.5 ± 0.14	1.4 ± 0.14	-10.12 ± 0.04	-5.52 ± 0.11
2	25	4.57 ± 0.35	7.03 ± 0.24	8.52 ± 0.41	2.45 ± 0.26	1.5 ± 0.36	-10.12 ± 0.35	-5.55 ± 0.35
3	30	4.7 ± 0.1	7.0 ± 0.1		2.3 ± 0.14		-10.7 ± 0.1	-6 ± 0.14
4	30	4.77 ± 0.51	7.47 ± 0.54	8.97 ± 0.58	2.7 ± 0.22	1.5 ± 0.22	-10.77 ± 0.5	-6 ± 0.1
4	30	4.77 ± 0.51	7.47 ± 0.54	8.97 ± 0.58	2.7 ± 0.22	1.5 ± 0.22	-10.77 ± 0.5	-6 ± 0.1
3	50	5.6 ± 0.2	6.9 ± 0.3	8.6 ± 0.3	1.3 ± 0.36	1.7 ± 0.42	-11.0 ± 0.1	-5.4 ± 0.22
4	50	5.7 ± 0.54	8.80 ± 0.57	10.30 ± 0.66	3.1 ± 0.18	1.5 ± 0.34	-11.1 ± 0.2	-5.4 ± 0.5
5	75	5.80 ± 0.58	8.80 ± 1.62	10.10 ± 1.42	3.0 ± 1.52	1.3 ± 1.41	-10.94 ± 0.29	-5.14 ± 0.51
4	75	5.2 ± 0.54	7.30 ± 0.61	8.90 ± 0.61	2.1 ± 0.28	1.6 ± 0.28	-10.5 ± 0.5	-5.3 ± 0.2
6	75	4.8 ± 0.28	7.20 ± 0.36	8.55 ± 0.56	2.40 ± 0.36	1.35 ± 0.42	-9.80 ± 0.2	-5.00 ± 0.2
7	75				2.2 ± 0.4	2.5 ± 0.45		-6.7 ± 0.2

ref.	°C	$\log_{10}K_{s1}\ \beta_2$	$\log_{10}K_{s1}\ \beta_3$	$\log_{10}K_{s2}$	$\log_{10}K_{s2}\ \beta_1$	$\log_{10}K_{s2}\ \beta_2$	$\log_{10}K_{s2}\ \beta_3$	$\log_{10}K_{s2} / K_{s1}$
1	25	-3.02 ± 0.11	-1.62					
2	25	-3.1 ± 0.24	-1.6 ± 0.41					
3	30	-3.70 ± 0.14						
4	30	-3.3 ± 0.2	-1.8 ± 0.3	-13.47± 0.55	-8.7 ± 0.24	-6.0 ± 0.1	-4.5 ± 0.2	-2.7 ± 0.22
4	30	-3.3 ± 0.2	-1.8 ± 0.3	-12.97 ± 0.62	-8.2 ± 0.37	-5.5 ± 0.41	-4.0 ± 0.2	-2.2 ± 0.36
3	50	-4.10 ± 0.32	-2.4 ± 0.32	-12.90 ± 0.22	-7.3 ± 0.3	-6.0 ± 0.37	-4.3 ± 0.37	-1.9 ± 0.2
4	50	-2.3 ± 0.53	-0.8 ± 0.59	-14.8 ± 0.55	-9.1 ± 0.1	-6.0 ± 0.15	-4.5 ± 0.3	-3.7 ± 0.51
5	75	-2.14 ± 1.60	-0.84 ± 1.39	-14.40 ± 1.15	-8.6 ± 0.99	-5.6 ± 1.14	-4.3 ± 0.83	-3.46 ± 1.12
4	75	-3.2 ± 0.35	-1.6 ± 0.35	-13.4 ± 0.57	-8.2 ± 0.2	-6.1 ± 0.2	-4.5 ± 0.2	-2.9 ± 0.28
6	75	-2.6 ± 0.3	-1.25 ± 0.52	-13.25 ± 0.47	-8.45 ± 0.47	-6.05 ± 0.3	-4.70 ± 0.3	-3.45 ± 0.42
7	75	-4.5 ± 0.45	-2.0 ± 0.63		-9.4 ± 0.63	-7.2 ± 0.4	-4.7 ± 0.2	-2.7 ± 0.6

Table [93LEM/BOY]2: ΔH estimation for Np(V) carbonate stepwise formation constants. ΔH_i ($kJ.mol^{-1}$) is the enthalpy variation corresponding to the $NpO_2(CO_{3i-1})^{3-2i} + CO_3^{2-} \Rightarrow NpO_2(CO_3)_i^{1-2i}$ reaction. There are calculated from the above k_i values as explained in the text.

t (°C)	Δt (°C)	ΔH_1	$\Delta H_1^{(a)}$	ΔH_2	$\Delta H_2^{(a)}$	ΔH_3	$\Delta H_3^{(a)}$
40	20	84 ± 21	87 ±70	-94 ± 37	37 ±27		0 ± 38
62.5	25	17 ± 55	-43 ±66	146 ±139	-86 ±29	-35 ±132	9 ± 38
52.5	45	49 ± 28	19 ±34	31 ± 74	-27 ±17		4 ± 16
25			19 ±138		-27 ±91		4 ± 42
25(b)			-15.9 ± 0.5		0.3 ± 0.5		

(a)Calculated by this review. (b)[96CLA/CON2].

25°C and 30°C. Following the authors, the solubility product tabulated above should not be compared with similar values from other works (at other temperature), since at least some of them do not correspond to the same solid phase even when X-ray characterisation was claimed. Lemire, Boyer and Campbell clearly indicated that there was problem with this type of characterisation, Vitorge et al. [84VIT and 89RIG] came to the same conclusion. The other authors used or showed X-ray characterisation mostly of initial solid phases.

From each stepwise complexing constant estimated by this review or by the authors a corresponding ΔH mean value was calculated by this review between each temperature (30 and 50°C, 50 and 75°C, and 30 and 75°C) corresponding to 40, 62.5 and 52.5°C. The uncertainty was calculated by usual propagation error rule from the uncertainty of k_i determinations at each temperature. The uncertainty was often much more than 100 %, so this review considered these calculations of estimations of maximum possible values and that no significative change of ΔH with temperature was estimated by this calculation. The proposed value at 25°C was the mean value, and the uncertainty was increased to overlap each determination (see the table). The β_1 value calculated from Lemire and Boyer's k_i determinations are of opposite sign from the estimation by this review, which are also of opposite singe of the later publication [96CLA/CON2] (that was not considered by this review); but all these numbers are in accord within uncertainty. Ionic strength corrections and ΔC_p influence (i.e. ΔH variations with T) are certainly much less than the uncertainty.

[94MEI]

Meinrath G. *Np(V) in carbonates in solid state and aqueous solution,* J. Radioanal. Nucl. Chem., Letters, 186, 3 (1994) 257-272.

Meinrath prepared a $NaNpO_2CO_{3(s)}$ compound by precipitating a 0.02 M NpO_2^+ acidic solution with 0.05 M Na_2CO_3. After three weeks of equilibration, he measured its solubility at 25°C bubbling a 1 % CO_2 (in N_2) gas mixture. Calibrating his glass electrode he determined the value $\log_{10}K_{p2} = 17.62 \pm 0.07$ for the carbonic gas / carbonate equilibrium constant. He rechecked it (17.65 ± 0.07) with Kim et al. later. The value calculated with the auxiliary thermodynamic data selected by this review is $\log_{10}K_{p2} = 17.53 \pm 0.04$. The author's address is at JAERI (Japan), but this paper is discussed in this appendix with other publications by Kim [91KIM/KLE and 94NEC/KIM] since Meinrath initially worked with Kim. As in a previous publication from Kim's laboratory [91KIM/KLE], Meinrath reproduced Vitorge's measurements. He determined the solubility product, K_{s1}, and the first carbonate complexing constant β_1. They are the same (within uncertainty) as the one previously published from Kim's laboratory [91KIM/KLE]. Since original solubility values were given in the [91KIM/KLE] report, and not in the [94MEI] publication, this review did not tried to evaluate Meinrath's results.

Meinrath claimed that he did not have all the solid phase problems that were extensively discussed by Vitorge [84VIT and 89RIG] and Lemire [93LEM/BOY] (see the discussion on the [84VIT, 89RIG 91KIM/KLE and 93LEM/BOY] in this appendix). There is not enough information to check this conclusion. This review the made same type of remark for the analysis of publication in Np(V) solubility in carbonate media by Kim's laboratory (see the discussion of the [91KIM/KLE and 94NEC/RUN]publications in this appendix).

[94NEC/KIM]

Neck V., Kim J.I., Kanellakopulos B. *Thermodynamisches Verhalten von Neptunium(V) in konzentrierten NaCl- und $NaClO_4$- Lösungen.* KfK 5301 February (1994).

This review used the Np(V) solubility measurements tabulated in this report, with other data published by the same group of authors (see the discussion of [91KIM/KLE and 94NEC/RUN] in this appendix). Experimental data of Np(V) liquid-liquid extraction by NaDNNS from 0.2 to 5 M Na^+, (ClO_4^-, Cl^-) aqueous carbonate solution are tabulated in this report. They were used by Neck, Kim and Kanellakopulos to estimate Np(V) activity coefficient. This review did not follow the interpretation of the authors as explained in this appendix when discussing a later publication [95NEC/FAN] from the same group using these experimental data. This review did not use either these experimental measurements to estimate the stability of Np(V) carbonate complexes because the needed activity coefficient and chloride complexing corrections increased the uncertainty of this interpretation, beside other systematic errors due to pH calibration as in similar work from this group (see the discussion of [91KIM/KLE and 94NEC/RUN] in this appendix).

[94NEC/RUN]

Neck V., Runde W., Kim J.I., Kanellakopulos B. *Solid-Liquid Equilibrium Reactions of Neptunium(V) in Carbonate Solution at Different Ionic Strength,* Radiochim. Acta, 65 (1994) 29-37.

Neck, Runde, Kim and Kanellakopulos added in this publication a few new solubility measurements that appeared in previous reports by the same group of authors and that were then examined elsewhere (see the discussion of the [91KIM/KLE and 94NEC/RUN] publications in this appendix). The new experimental results were Np(V) solubility measurements in 5 M NaCl carbonate aqueous solutions, and figures showing the transformation of the $NaNpO_2CO_{3(s)}$ initial hydrated phase into a $Na_3NpO_2(CO_3)_{2(s)}$ one. Np(V) concentration was measured during this solid phase transformation; but it seems that they were not plotted on the figures (possibly because they were clearly not obtained in equilibrium conditions). Still the shape and the scattering of the experimental curves in 5 M NaCl media are consistent with the interpretation of Lemire concerning solid phase transformation (see the discussion of the [93LEM/BOY] publication in this appendix); namely two hydrated forms with $Na_3NpO_2(CO_3)_{2(s)}$ stoichiometry as also previously suggested in 3 M $NaClO_4$ media (see the discussion of the [89RIG] publication in this appendix) and possibly the formation of a new solid phase with intermediary stoichiometry. As already inferred by this review about Kim's group publication (see the discussion on the [91KIM/KLE] report in this appendix), these small problems were usually not seen on the publications probably because the authors did not report the experimental data that they considered as outlier (or possibly not at equilibrium).

The other new data proposed in this [94NEC/RUN] work was activity coefficient. In this publication the SIT as proposed by this review, was used by Neck, Runde, Kim and Kanellakopulos; while in a later work [95FAN/NEC] they used a simplified Pitzer equation. As already mentioned elsewhere in this appendix (see the discussion of the [91KIM/KLE and 94NEC/RUN] publications), there was possibly a systematic deviation in $[CO_3^{-2}]$ determination (from pH measurement) since the carbonic gas acidic constant redetermined for the glass electrode calibration, was not consistent with published values, neither with the value calculated with the auxiliary data selected by this review. Junction potential was measured (and not set to zero by using the same ionic medium for the reference electrode and working solutions). The interpretation of the liquid-liquid extraction studied neglected the activity coefficient correction in the organic phase. These corrections and systematic errors were quite important when compared to activity coefficient corrections. The corresponding uncertainty could not be deduced from statistical analysis since some of the possible errors were systematic (not at random). In addition possible chemical systematic error (discussed above) could be even more important. For these reasons, this review did not consider the activity coefficients proposed in this [94NEC/RUN] work. On the other hand as already mentioned elsewhere in this appendix (see the discussion of the [91KIM/KLE and 94NEC/RUN] reports), some of the systematic errors cancel, specially for the values of equilibrium constants extrapolated to zero ionic strength. The $\Delta\varepsilon$ value of the solubility products can be calculated from ε values used by this review (see the appendix B) that were determined from isopestic (for $\varepsilon(Na^+,ClO_4^-)$) , equilibrium constants (for $\varepsilon(Na^+,CO_3^{-2})$) and redox (for $\varepsilon(NpO_2^+,ClO_4^-)$) measurements. For this last value analogy between NpO_2^{+2} and UO_2^{+2} were also assumed since the experimental determinations of the $\Delta\varepsilon$ values of the MO_2^{+2}/MO_2^{+2} redox couples were found to be the same for M = U, Np, Pu, Am [87RIG/VIT, 89RIG, 89RIG/ROB and 94CAP/VIT]. The $\Delta\varepsilon$ value of the two solubility products determined by Kim's group [91KIM/KLE and 95NEC/RUN] are not consistent with the value calculated by this review (see the table). The two $\varepsilon(NpO_2^+,ClO_4^-)$ calculated from Kim's $\Delta\varepsilon$ values are not consistent with later determination by the same group

Table KIM2: $\varepsilon(NpO_2^+,ClO_4^-)$ deduced from the measurements of Kim's group. ε is $\varepsilon(NpO_2^+,ClO_4^-)$. $\Delta\varepsilon_{si} = i\ \varepsilon(Na^+,CO_3^{-2}) + \varepsilon + (2\ i - 1)\ \varepsilon(Na^+,ClO_4^-) + x_i\ r$ were determined by SIT linear regression from the values determined at different ionic strength for K_{si}, the $Na_{2i-1}NpO_2(CO_3)_{i(s)}.x_iH_2O$ solubility product, where r is a_{H2O} / m_{NaClO4} mean value, x_1 = 3.5 and x_2 is unknown. Two arbitrary x_2 values were then used (see the footnotes). The ε and Δε values calculated with the auxiliary values used by this review (see the text and the appendix B) are tabulated in the TDB column. All the other values are deduced from Kim et al. experimental measurements (referred in the first line). Comparison of the different ε determination shows internal inconsistency between the values determined by Kim's group. Most of his ionic strength correction that he used for his solubility products is neither consistent with the well-known values (TDB column).

	TDB	[91KIM/KLE]	[95NEC/RUN]	0.1 to 3 M[c]	0.1 to 5 M[c]	[95NEC/FAN]
$\Delta\varepsilon_{s1}$	0.13 ± 0.06	0.24 ± 0.03	0.22 ± 0.03	0.26 ± 0.06	0.26 ± 0.01	
$\Delta\varepsilon_{s2}$	0.12 ± 0.08		0.24 ± 0.08			
$\Delta\varepsilon_{ss}^a$	-0.01 ± 0.04		0.02 ± 0.09			
$\Delta\varepsilon_{ss}^b$	-0.06 ± 0.04		0.02 ± 0.09			
ε	0.25 ± 0.05	0.36 ± 0.04	0.34 ± 0.04	0.38 ± 0.07	0.38 ± 0.04	0.20[e] ± 0.03
$\varepsilon^{a,d}$			0.37±0.09			
$\varepsilon^{b,d}$			0.42±0.09			
$\log_{10}K_{s1}$				-10.95 ±0 .11	-10.95 ± 0.07	

[a]Assuming x_2 = 0 in the solid phase. [b]Assuming x_2 = 3.5. [c]Calculated by this review from the data reported in [91KIM/KLE]. [d]Calculated from K_{s2}. [e]Calculated by this review from the Pitzer set of parameters proposed in the [95NEC/FAN] publication.

[95NEC/FAN]: a simplified (correct) Pitzer equation was used from which this review determined $\varepsilon(NpO_2^+,ClO_4^-)$ = 0.21 which is in accord with the values accepted by this review (see the table).

Kim's group ionic strength corrections are then not self consistent. The ones he used for solubility products are neither consistent with well-known ε coefficients. These two inconsistencies of Kim's solubility works could be due to the small systematic error that this review noticed in this appendix: the theoretical methodology was not completely correct, $[CO_3^{-2}]$ experimental determination possibly in error at high ionic strength and chemical problems with the solid phases were possibly not completely reported.

[95FAN/NEC]

Fanghänel Th., Neck V., Kim J.I. *Thermodynamic of Neptunium(V) in Concentrated Salt Solutions: II. Ion Interaction (Pitzer) Parameters for Np(V) Hydrolysis Species and Carbonate Complexes,* Radiochim. Acta, 69 (1995) 169-176.

See the discussion of the [91KIM/KLE 94NEC/KIM, 94NEC/RUN and 96RUN/NEU] reports and publications in this appendix.

[95NEC/FAN]

Neck V., Fanghänel Th., Rudolph G., Kim J.I. *Thermodynamic of Neptunium(V) in Concentrated Salt Solutions: Chloride Complexation and Ion Interaction (Pitzer) Parameters for the NpO_2^+ Ion,* Radiochim. Acta, 69 (1995) 169-176.

See the discussion of the [91KIM/KLE 94NEC/KIM and 94NEC/RUN] reports and publications in this appendix.

[95NEC/RUN]

Neck V., Runde W., Kim J.I., Kanellakopulos B. *Solid-liquid equilibria of neptunium(V) in carbonate solution of different ionic strengths: II. Stability of the solid phases,* Radiochim. Acta, 65 (1994) 29-37.

See the discussion of the [91KIM/KLE 94NEC/KIM and 94NEC/RUN] reports and publications in this appendix.

[96CLA/CON]

Clark, D.L., Conradson, S.D., Ekberg, S.A., Hess, N.J., Neu, M.P., Palmer, P.D., Runde, W., Tait, C.D. *EXAFS studies of pentavalent neptunium carbonato complexes. Structural elucidation of the principal constituents of neptunium in groundwater environments*, J. Am. Chem. Soc., 118 (1996) 2089-2090.

This is an interesting paper that proposes bound lengths in the $NpO_2(CO_3)_i^{1-2i}$ aqueous complexes from EXAFS studies, assuming reasonable geometry of these species. Tetrabutylamonium cation instead of usual alkali ones, where used as supporting electrolyte when fixing the aqueous speciation: this is a classical way to avoid precipitation of the Np(V) with alkali cations. No information from this publication was used by the present revue.

[96CLA/CON2]

Clark, D.L., Conradson, S.D., Ekberg, S.A., Hess, N.J., Janecky, D.R., Neu, M.P., Palmer, P.D., Tait, C.D. *A multi-method approach to actinide speciation applied to pentavalent neptunium carbonate complexation* New J. Chem., 20 (1996) 211-220.

This is mostly a review paper mainly based on experimental observation of the authors and literature comparison that they previously published. Still, Clark et al. reported new results of their experimental study of the temperature influence on the $NpO_2CO_3^-$ and $NpO_2(CO_3)_2^{-3}$ formation constants. β_1 and β_2 were measured in 0.1 M $TBANO_3$ aqueous solution (TBA is tetrabutylamonium) by spectrophotometry, possibly as in the[94NEC/RUN] publication; but the spectrophotometric results of this publication were not much accurate and were not considered by the present review (see the discussion of the [94NEC/RUN] publication in this appendix). Clark et al. found that $\log_{10}\beta_1$ and $\log_{10}\beta_2$ increased by about 0.4 unit $\log_{10}$ from 30 to 70°C, while they estimated 0.2 $\log_{10}$ unit uncertainty on the $\log_{10}\beta_1$ value. Temperature influence was then not much more than the experimental accuracy as earlier found by Lemire [93LEM/BOY]. They plotted $\log_{10}\beta_1$, $\log_{10}\beta_2$ and

$\log_{10}k_2$ ($k_2 = \beta_2/\beta_1$) as a function of 1/T, and observed straight lines with slopes 829±27, 811 and 18 respectively, from which ΔH_1 = -15.9±0.5 kJ.mol.$^{-1}$, ΔH_2 = -15.5±0.5 kJ.mol.$^{-1}$ and then $\Delta H_2 - \Delta H_1$ = -0.3±0.5 kJ.mol.$^{-1}$ respectively. These results were not considered by the present review since the information needed to check them were not reported in this publication [96CLA/CON2].

[96FAN/NEC]

Fanghänel Th., Neck V., Kim J.I. *The Ion Product of H_2O, Dissociation Constants of H_2CO_3, and Pitzer Parameters in the System $Na^+/H^+/OH^-/HCO_3^-/CO_3^{-2}/ClO_4^-/H_2O$ at 25°C* J. Sol. Chem., 25, 4 (1996).

As this review was finished, this paper came to the knowledge of the reviewer. It contains supplementary information on the calibration procedure used by these authors for their glass electrode. As discussed elsewhere in this appendix, systematic deviation was suspected by this review. The authors said that instead of the theoretical Nernstian slope (59.16 mV/$\log_{10}a_{H^+}$ at 25°C), they found 58.0 to 58.8 mV. The author should have solved this problem prior to any other measurements, it is often due to instability of the reference electrode. This might also be due to alkaline error in glass electrode response (but it is usually important at higher pH than used in this work). All the treatment of the data that followed might then be completely empirical. The deviation is not much important, but it confirms the opinion of this review that suspected systematic deviation in the calibration procedure used by that laboratory. Anyhow the K_w results are in accord with the thermodynamic data selected by this review and with experimental determination cited in a previous paper from the same laboratory [94NEC/RUN]. Their determinations of the carbonic acid acidity constants are in accord with previous determination from the same laboratory [94NEC/RUN], and then again deviates from published values at high ionic strength. This problem was recognised in the present paper [96FAN/NEC] and attributed to possible non-Nernstian slope of glass electrodes for other publications: as they found this systematic deviation in their [96FAN/NEC] work and corrected it empirically, they assumed that other authors should have used the same empirical procedure. This is a possible assumption; but as explained above, to attribute systematic error to nearly all the rest of the literature (including laboratories that were well known to set up proper methodology, while the present group of authors started only quite recently to perform ionic corrections: see the discussion on other Kim's paper in this appendix), to accept the explanation of the authors, the present review would have need more checking on the glass electrode used in this [96FAN/NEC] work: other glass electrodes could have been tested (this is classical), and other (more classical methodology) could have been used, specially experimental set up with junction potential less than uncertainty... For this reason, this review did not consider these data at high ionic strength. Still, as already noticed (see the discussion of other Kim's et al. papers in this appendix), these deviations were quite small and certainly cancelled at low ionic strength. They are not completely understood by the present review.

[96RUN/NEU]

Runde W., Neu, M.P., Clark, D.L. *Neptunium(V) hydrolysis and carbonate complexation: Experimental and predicted neptunyl solubility in concentrated NaCl using the Pitzer approach.* Geochim. Cosmochhim. Acta, 60 (1996) 2065-2073.

This paper reports a few new experimental results. Runde, Neu and Clark proposed some new Pitzer parameters to calculate the mean activity coefficients, $\gamma_\pm$, of Np(V) species with ClO_4^-, Cl^- or Na^+ conter ion. The numerical values proposed here [96RUN/NEU] to calculate the NpO_2ClO_4 and NpO_2 Cl $\gamma_\pm$ are a little different from the set of values determined earlier [95NEC/FAN]; but this review calculated the SIT coefficients $\varepsilon(NpO_2^+,ClO_4^-)$ = 0.18±0.02 and 0.20±0.03 from the Pitzer parameters of these two publications, [96RUN/NEU and 95NEC/FAN] respectively, which is in accord with the value used by this review (see the discussion of the [94NEC/RUN] publication in this appendix). In the same way this review calculated from the Pitzer parameters reported in the [96RUN/NEU] publication: $\varepsilon(NpO_2^+,Cl^-)$ = 0.09±0.01; but this value includes the effect of formation of Np(V) chloride complex, it cannot then be consistent with the thermodynamic description used by the present review; $\varepsilon(Na^+,NpO_2(OH)_2^-)$ = -0.12±0.05 which seems reasonable; but unbelievable values for $\varepsilon(Na^+,NpO_2(CO_3)_2^{-3})$ and $\varepsilon(Na^+,NpO_2(CO_3)_3^{-5})$. To be consistent with this approximation, this review only used the 1-1 Pitzer interaction coefficients, while they had been fitted together with other parameters whose effect should be less than the SIT accuracy. This procedure had been tested for 1-1 electrolyte [95OFF/CAP pages 27-38] and was again tested for those for which Pitzer parameters are tabulated in this [96RUN/NEU] publication and for Na_2CO_3: the ε coefficients calculated in this way had the expected values (tabulated in the appendix B). As for previous works [95NEC/FAN] the problem is not in using Pitzer equation (it was anyhow readily converted into the corresponding SIT ε coefficient); but in the selection of the experimental data, because usual scattering of the published experimental data, is of the order of magnitude of ionic strength corrections; and in the curve fitting procedure because activity coefficient and complexing constants are correlated. This means that one can fit several sets of these parameter values, that account for the experimental data, practically as well; but not all of them have the assumed chemical and physical meaning. To avoid this problem, extra information must be include in the curve fitting procedure, the most usual one is to fit independently each equilibrium constant in conditions where activity coefficients are reasonably constant, prior to the activity coefficient calculations. Anyhow this publication did not contain enough experimental information to allow checking of these new ε values, and of the type of problems discussed in this appendix for the [91KIM/KLE] work.

Runde, Neu and Clark also proposed new Np(V)-CO_3 solubility product and complexing constants in 0.1 and 3 M NaCl aqueous solutions. To eliminate the effect of chloride complexation, this review tabulated only stepwise complexing constants, and anyhow did not used them because this publication does not give the needed information to allow checking besides the other problems discussed elsewhere in this appendix for similar work by the first author who published with Kim (see the discussion of the [91KIM/KLE and 94NEC/KIM publications in this appendix).

Supplementary materials

Np(V)-OH-CO_3 data presented at the Migration'91 conference

First line of each table block indicates the name of the constant published and reinterpreted (in this work) $\log_{10}$ of constants and their uncertainties (±) are tabulated. Experimental methods of measurement are: electromigration (el.mig), literature review (lit), potentiometry (pot), pulse radiolysis (p.rad), solubility (sol), spectrophotometry (sp). Selected values (select) are the standard values deduced in the present work (p.w.) from SIT extrapolation (SIT) to 0 ionic strength, they are on the same line as the name of the constant in "reinterpreted column", when (SIT) is not indicated in the "method" column (of this first line) no selected value is proposed. When inequalities are indicated, this means that this review could only estimate a maximum possible value for the equilibrium constant.

$^*\beta_i$ = $[NpO_2(OH)_i^{1-i}][H^+]^i / [NpO_2^+]$
$^*Ks_i$ = $[M^+]^i [NpO_2^+] / [H^+]^{i+1}$, is $M_iNpO_2(OH)_{i+1(s)}$ solubility product
$^*ks_i$ = $[M^+] / [H^+]$ = $^*Ks_i / ^*Ks_{i-1}$
β_i = $[NpO_2(CO_3)_i^{1-2i}] / [NpO_2^+] [CO_3^{2-}]^i$
Ks_i = $[M^+]^{2i-1} [NpO_2^+] [CO_3^{2-}]^i$ is $M_{2i-1}NpO_2(CO_3)_{i(s)}$ solubility product
$^*\beta_{i;j}$ = $[NpO_2)CO_3)_i(OH)_j^{1-2i-j}] [H^+]^j / [NpO_2^+] [CO_3^{2-}]^i$

OH^- equilibrium constants

This table was given to the Np- Pu group of the TDB, where Robert Lemire is in charge of Np hydrolysis. He then performed more reviewing on this subject, and this table was an internal working document (not the result of the final selection of thermodynamic data).

		±	reinterpreted	±	I	medium	method	ref.
$^*\beta_1$			< -11		0		lit	p.w.
	-8.9	0.1	< -9		0.1	Cl^-	pot	[48KRA/NEL]
	-10.1		< -10			diluted	sol	[71MOS3]
	-8.92	0.04	< -9		0.02	HNO_3	pot	[76SEV/KHA]
	-8.9	0.1	$NpO_2CO_3^-$				spec	
	-8.94	0.05	< -9		0.02	$HClO_4$	pot	
	-8.7	1.0	< -9		0.01	EtOH	p.rad	[80SCH/GOR]
			< -13 ?		0 to 0.1	NaOH	sol	[85EWA/HOW]
	-11.7	0.62	< -11.3		1	$NaClO_4$	sol	[85LIE/TRE]
	-10.45	0.25	?		0.1	$NaClO_4$	el.mig	[87ROE/MIL]
	-8.3		< -8		0.01	$NaNO_3$	sol	[88NAK/ARI]
$^*\beta_2$			< -23		0		lit	p.w.
	-23.11	0.05	NpO_2-CO_3 ?		1	$NaClO_4$	sol	[85LIE/TRE]
	-21.95	0.35	?		0.1	$NaClO_4$	el.mig	[87ROE/MIL]
	-19.4		NpO_2-CO_3		0.01	$NaNO_3$	sol	[88NAK/ARI]
$^*K_{s0}$			5.12	0.34				p.w.
	4.8	0.3	4.8	0.5	0.00032		sol	[48KRA/NEL]
	4.97	0.07	5.0	0.3		diluted	sol	[71MOS3]
	5.08	0.04	5.1	0.3		HNO_3 diluted.	sol	[76SEV/KHA]
	3.8		3.9	1.2	9	NaOH + ?	sol	[78MUS]
					0.02 to 2.1	NaOH	prep	[84VIS/VOL]
			4.6	0.4	0 to 0.1	NaOH	sol	[85EWA/HOW]
	5.19	0.05	5.0	0.3	1	$NaClO_4$	sol	[85LIE/TRE]
	3.3		3.3	0.5	0.01	$NaNO_3$	sol	[88NAK/ARI]
$^*k_{s1}$								
			13.4	1.1	2.1 to 15	NaOH	prep.	[84VIS/VOL]
			13.6	1.2	3.5 to 9	KOH	prep.	
$^*k_{s2}$								
			13.5	1.5	15	NaOH	sol	[84VIS/VOL]
			15.5	1.3	9	KOH	sol	
$^*K_{s2}/^*K_{s0}$								
			13.8	1.1	2	LiOH	sol	[84VIS/VOL]

CO_3 equilibrium constants.

This table was in the first draft of the TDB book, Neptunium and Plutonium Chemical Thermodynamics.

		±	reinterpreted	±	I	medium	method	ref.
β_1			**4,70**	0.10	0		SIT	p.w (select)
			5.5	0.5	0.02		sp	[81BIL]
	4.49	0.06	4.56	0.3	1	$NaClO_4$	sol	[83MAY]
	4.13	0.03	3.9	0.5	0.2	$NaClO_4$	ext	[85BID/TAN]
	4.14	0.01	4.14	0.5	1	$NaClO_4$	ext	[85INO/TOC]
			5.34	0.13	3	$NaClO_4$	sol	[86GRE/ROB] and p.w

	±	reinterpreted	±	I	medium	method	ref.
4.62				0			[86GRE/ROB]
4.39	0.04	4.39	0.2	0.5	$NaClO_4$	sp	[89RIG]
4.3	0.1						
β_2		**6.39**	0.21	0		SIT	p.w (select)
7.11	0.07	7.13	0.2	1	$NaClO_4$	sol	[83MAY]
7.06	0.05	7.06	0.5	0.2	$NaClO_4$	ext	[85BID/TAN]
6.78	0.01	6.78	0.5	1	$NaClO_4$	ext	[85INO/TOC]
		8.13	0.6	3	$NaClO_4$	sol	[86GRE/ROB] and p.w
6.93				0			[86GRE/ROB]
β_3		**5.52**	0.33	0		SIT	p.w (select)
8.53	0.09	8.54	0.3	1	$NaClO_4$	sol	[83MAY]
		10.56	0.18	3	$NaClO_4$	sol	[86GRE/ROB] and p.w
5.86				0			
$\beta_{2,2}$				3	0.1toNa_2CO_3,	spec	p.w.
-17.0	0.6				0.1 to 1 NaOH ($NaClO_4$)		
k_2		1.38	0.32	0		SIT	p.w (select)
		2.5	0.5	0.1	$NaHCO_3$ < 0.13	copr	[79MOS/POZ]
		2.5	0.5	0.01		sp	[81BIL]
2.62	0.13	2.57	0.5	1	$NaClO_4$	sol	[83MAY]
2.93	0.08	3.16	1	0.2	$NaClO_4$	ext	[85BID/TAN]
2.64	0.02	2.64	1	1	$NaClO_4$	ext	[85INO/TOC]
		2.79	0.6	3	$NaClO_4$	sol	[86GRE/ROB] and p.w
2.31				0			[86GRE/ROB]
		2.75	0.5	3	Na_2CO_3 0.02 to	sp	[89RIG]
2.54	0.07	2.5	0.3	2	0.4		
2.05	0.07	2.45	0.15	2	($NaClO_4$)		
2.38	0.07	2.05	0.5	1			
2.23	0.07	2.1	0.6	0.5			
1.51	0.15			0			
		1.4	0.3	0.03	Na_2CO_3		
k_3		-0.86	0.13	0		SIT	p.w (select)
		0.7	0.2	0.2	$(NH_4)_2CO_3$	sol	[71MOS5]
		1.2	0.3	0.06	Na_2CO_3	sol	[75UEN/SAI]
		1.4	1	0.2		sp	[81BIL]
1.42	0.16	1.41	0.5	1	$NaClO_4$	sol	[83MAY]
		2.43	0.6	3	$NaClO_4$	sol	[86GRE/ROB] and p.w
-1.07				0			[86GRE/ROB]
2.47	0.07			2	Na_2CO_3 0.02 to	sp	[89RIG]
1.86	0.07			1	0.4		
1.60	0.07	1.91	0.11	1	($NaClO_4$)		
1.37	0.07			0.5			
-0.86	0.15			0			
-0.98	0.15			0			
		1.00	0.04	0.1	Na_2CO_3		
$\beta_{2;2}/\beta_3$				3	0.1 toNa_2CO_3,		
-27.5	0.5	-27.5	0.5		0.1 to 1 NaOH ($NaClO_4$)	spec	p.w
K_{s1}		**-11.00**	0.22	0		SIT	p.w (select)
-10.14	0.04	-10.13	0.12	1	$NaClO_4$	sol	[83MAY]
		-11.11	0.09	3	$NaClO_4$	sol	[86GRE/ROB]+pw
K_{s1} β_1		-6.06	0.18	0		SIT	p.w (select)
-5.65	0.06	-5.57	0.50	1	$NaClO_4$	sol	[83MAY]
		-5.77	0.09	3	$NaClO_4$	sol	[86GRE/ROB]+pw
K_{s1} β_2		-4.31	0.29	0		SIT	p.w (select)
-3.03	0.07	-3.00	0.15	1	$NaClO_4$	sol	[83MAY]
		-2.98	0.59	3	$NaClO_4$	sol	[86GRE/ROB]+pw
K_{s1} β_3		-5.60	0.23	0		SIT	p.w (select)
		-2.3	0.3	0.16	K_2CO_3	sol	[66GOR/ZEN]
		-3.3	0.3	0.3	$(NH_4)_2CO_3$	sol	[71MOS5]
		-2.5	0.3	0.1	Na_2CO_3	sol	[75UEN/SAI]
		-1.6	0.3	0.6			

	±	reinterpreted	±	I	medium	method	ref.
-1.61	0.09	-1.59	0.20	1	$NaClO_4$	sol	[83MAY]
		-0.55	0.14	3	$NaClO_4$	sol	[86GRE/ROB]+pw
$K_{s2}\ \beta_3$							
		-2.9	0.3	1	K_2CO_3	sol	[66GOR/ZEN]
		-3.4	0.3	0.7	$(NH_4)_2CO_3$	sol	[71MOS5]
		-1.5	0.3	3	$NaNO_3$	sol	[77SIM]
$^*\beta_{0;1}$		<-9		3	$NaClO_4$	sol	[86GRE/ROB]+pw
-9.12	0.15	<-10		1	$NaClO_4$	sol	[83MAY]
-9.84		<-9		0.2	$NaClO_4$	ext	[85BID/TAN]
$^*\beta_{1:-1}$		<10		3	$NaClO_4$	sol	[86GRE/ROB]+pw
8.1							[63MOS/GEL]
7.9				0			
11.7				0.25	$NaHCO_3$	copr	[79MOS/POZ]
12.52				0			
$^*\beta_{1:1}$		<<-9		3	$NaClO_4$	sol	[86GRE/ROB]+pw
-9.18	0.12			0 to 2.2	$(NH_4)_2CO_3$	sol	[71MOS5]
$^*\beta_{1:2}$		<<0					[86GRE/ROB]+pw
$^*\beta_{2:-1}$		<15					[86GRE/ROB]+pw
$^*\beta_{2:1}$		<-3		3	$NaClO_4$	sol	[86GRE/ROB]+pw
-9.26	0.05			0 to 2.2	$(NH_4)_2CO_3$	sol	[71MOS5]
$^*\beta_{3:-1}$		<21					[86GRE/ROB]+pw
$^*\beta_4$		<10					[86GRE/ROB]+pw

Standard equilibrium constants and SIT coefficients, ε

"Slope result" is Δε calculated from linear (SIT) regression corresponding to the equilibrium constant, K. E refers to redox measurements [89RIG/ROB]. Calculated ε is deduced from calculated Δε and published ε [89RIG] [92GRE/FUG] (in select. column with no other value on the same line). Different ε determinations are compared to propose a selected value (select.) which is then use to deduce calculated Δε ($mol.kg^{-1}$). These coefficients are for $NaClO_4$ media.

		slope result		calculated				select.	
	K	Δε	±	Δε	±	ε	±	ε	±
NpO_2^+	E	0.21	0.03			0.26	0.08	0.26	0.08
	$^*Ks_0$			0.24	0.08				
	Ks_1	0.28	0.10	0.22	0.12	0.32	0.14		
NpO_2OH^0	$^*Ks_1$			0.00				0.00	
$NpO_2(OH)_2^-$	$^*Ks_2$								
$NpO_2CO_3^-$	$Ks_1\ \beta_1$	0.00	0.06	-0.06	0.08	-0.01	0.07	-0.07	0.07
	K_1	-0.40	0.03	-0.28	0.18	-0.19	0.14		
$NpO_2(CO_3)_2^{3-}$	$Ks_1\ \beta_2$	-0.12	0.07	-0.15	0.13	-0.18	0.11	-0.21	0.09
	k_2	-0.13	0.03	-0.09	0.19	-0.25	0.13		
$NpO_2(CO_3)_3^{5-}$	$Ks_1\ \beta_3$	-0.29	0.04	-0.25	0.15	-0.40	0.11	-0.36	0.08
	k_3	-0.04	0.02	-0.06	0.20	-0.30	0.14		
$NpO_2(CO_3)_2(OH)_2^{5-}$	$^*\beta_{2,2}/\ \beta_3$	0.85	0.50	0.88	1.19			-0.36	0.20

	OH^-	ClO_4^-	CO_3^{2-}	H^+	Li^+	Na^+	K^+	UO_2^{2+} (NpO_2^{2+})
ε	0.04±0.01	0.01±0.01	-0.05*±0.03	0.14±0.02	0.15±0.01	0.01±0.01	0.01±0.02	0.46±0.03

*This value has been changed, it is now -0.08 [95SIL/BID].

Solubility and sensitivity analysis

This experimental work was proposed by *Ingmar Grenthe* (KTH, Stockholm), he came with *Diego Ferry* for helping to start the solubility measurements under CO_2 bubbling. They were performed by *Christian Dautel*. T = 20±1°C. $[Na^+]$ = 3M, in ClO_4^- media. The solubility, $[Np]_{total}$, and $-lg[H^+]$ were measured either in a cell where P_{CO_2} was controlled by bubbling CO_2 - N_2 gas mixture for the 65 first points (n = 1 to 65), or in batches where $[CO_3]_t$, the CO_3 total concentration, is known from the $NaHCO_3$ or Na_2CO_3 quantity added.

$$\log_{10}[CO_3^{2-}] = \log_{10}P_{CO_2} - 2\log_{10}[H^+] - 17.62$$
$$= [CO_3]_t \,/\, (1 + 10^{9.62+\log_{10}[H^+]}\,(1 + 10^{6.37+\log_{10}[H^+]})).$$

The 65 first points are in chronological order, the time (hour) was set to 0 when CO_2 bubbling was stooped (several days); but the solution and the solid in it, were not removed (and were then used again for the following points). Some points(*) are (a priori) not considered in the treatment of the data, because the experiment is still starting (start), or solubility where not stable for constant solution conditions (wait), or CO_2 stopped bubbling (CO2), or pH was too low to be stable in batches (l. pH), or was not buffered (buf.) or solid phase was changing (solid). Several precipitations and dissolutions are performed in the cell, noted respectively Pi and Di (in the n2 column). Some batches (those with the same n2 number) have been sampled at 2 different times. X ray diffraction results (RX) are named as in the following tables: 1 for $NaNpO_2CO_{3(s)}$, 2 for $Na_3NpO_2(CO_3)_{2(s)}$, and am for amorphous phase. These experimental data are the same as in the [84VIT,85COM, 85KIM, 86GRE/ROB and 89RIG] works. c is $[CO_3^{2-}]$.

n	hour	n1	n2	$-\lg[H^+]$	-lg c	$-\lg[Np]_t$		RX	n	hour	n1	n2	$-\lg[H^+]$	-lg c	$-\lg[Np]_t$		RX
1	24			5.10	7.40	3.97	*start		34	692	24	P2	6.98	4.55	5.72		
2	101			5.10	7.40	3.90	*start		35	716	25	P2	6.95	4.61	5.61		
3	151			5.09	7.45	4.48	*start		36	787		P2	7.00	4.44	5.80	*CO2	
4	264	1	P1	5.85	5.93	5.02			37	793		P2	7.00	4.51	5.55	*CO2	
5	439	2	P1	6.21	5.21	5.40			38	817	26	P2	6.94	4.63	5.76		1d
6	534	3	P1	6.63	4.37	5.70			39	955	27	P2	7.33	3.78	5.62		
7	648	4	P1	6.36	4.91	5.62			40	985	28	P2	7.25	3.94	5.61		
8	792	5	P1	6.58	4.47	5.71			41	1031	29	P2	7.25	3.94	5.59	wait	1a
9	864	6	P1	6.54	4.55	5.70			42	1128	30	P2	7.06	4.32	5.80	wait	
10	1157	7		6.64	4.35	5.55	CO2		43	1147	31	P2	7.07	4.30	5.78	wait	
11	0			6.62	4.39	5.35	*start		44	1219	32	D2	6.65	5.27	5.57		
12	50			6.53	4.57	5.59	*start		45	1291	33	D2	6.62	5.33	5.55		
13	120			6.44	4.75	5.60	*start		46	1321	34	D2	5.92	6.73	4.36	wait	
14	150			6.29	5.07	5.57	*start		47	1363	35	D2	5.94	6.69	4.35		
15	192	8	D1	5.99	5.65	4.98	start		48	1392	36	D2	5.36	7.85	3.28		
16	264	9	D1	5.58	6.47	4.44	start		49	4			5.42	7.73	3.30	*start	
17	295		D1	5.08	7.47	3.62	*wait		50	29			5.46	7.65	3.27	*start	
18	312	10	D1	5.12	7.39	3.48	start		51	173	37		5.10	8.37	2.62	start	1a
19	341	11	D1	4.73	8.17	2.82	start		52	282	38	P3	4.51	8.61	2.61		
20	432	12	D1	4.78	8.07	2.82	start		53	367	39	P3	4.87	7.89	3.32		
21	439	13	D1	4.72	8.19	2.85			54	431	40	P3	4.86	7.91	3.32		
22	456	14	D1	4.73	8.17	2.81		1d	55	484	41	P3	5.34	6.95	4.32		
23	120		P2	5.58	7.42	3.54	*start	1b	56	527	42	P3	5.35	6.93	4.34		
24	164	15	P2	5.57	7.44	3.57			57	576	43	P3	5.68	6.27	5.07	wait	
25	215	16	P2	5.96	6.66	4.41			58	647	44	P3	5.45	6.73	4.42		
26	312	17	P2	6.23	6.12	4.83			59	695	45	P3	5.97	5.69	5.34		
27	384	18	P2	6.39	5.80	5.21			60	767	46	P3	5.95	5.73	5.06		
28	456	19	P2	6.77	4.97	5.63			61	815	47	P3	5.95	5.73	5.34		
29	459	20	P2	6.66	5.19	5.57			62	935	48	P3	6.36	4.91	5.68		
30	500	21	P2	6.65	5.21	5.61		1c	63	1032	49		6.36	4.91	5.47		
31	548		P2	6.82	4.87	5.43	*wait		64	1175	50		5.85	5.93	5.24		
32	620	22	P2	6.82	4.87	5.72			65	1206	51		5.46	6.71	4.62		
33	644	23	P2	6.83	4.85	5.72											
66	672		1	7.65	5.95	4.92	*l. pH		76	1344		1	6.70	7.02	4.88	*l. pH	
67	672		2	7.80	5.37	5.68	*l. pH		77	1344		2	7.70	5.46	4.90	*l. pH	
68	672	52	3	9.10	3.86	5.86			78	1344		3	8.80	4.11	5.23	*buf.	
69	672	53	4	9.60	3.14	5.72			79	1344	57	4	9.60	3.14	5.79		
70	672	54	5	9.80	2.62	5.26			80	1344	58	5	9.72	2.66	5.17		
71	672	55	6	10.20	2.06	4.48			81	1344	59	6	10.12	2.08	4.50		
72	672	56	7	10.52	1.57	3.66			82	1344		7	10.43	1.59	4.54	*solid	
73	672		8	10.65	1.04	4.30	*solid	2	83	1344		8	10.60	1.04	4.43	*solid	
74	672		9	7.85	5.74	4.86	* l.pH	1	84	1344		9	7.80	5.74	4.57	* l. pH	
75	672		10	7.80	6.35	5.73	* l.pH		85	1344		10	8.00	6.12	5.42	* l. pH	
86	672		11	10.50	1.05	3.83	*		101	336		26	7.91	3.74	5.59	* solid	
87	672	60	12	10.50	1.27	3.08			102	336		27	8.32	3.53	5.64	* solid	
88	672	61	13	10.43	1.46	3.44			103	336		28	8.30	3.75	5.78	* solid	
89	672	62	14	10.43	1.70	3.90			104	336		29	8.28	3.98	5.59	* solid	
90	672	63	15	10.36	1.85	4.13			105	336		30	8.25	4.20	5.78	* solid	am
91	672	64	16	10.33	2.08	4.48			106	504		31	8.20	3.45	5.57	* solid	am
92	672	65	17	10.27	2.29	4.81			107	504		32	8.30	3.58	5.70	* solid	
93	672	66	18	10.15	2.51	5.04			108	504		33	8.25	3.80	5.59	* solid	
94	672	67	19	10.04	2.75	5.40			109	504		34	8.21	4.08	5.78	* solid	
95	672	68	20	9.94	2.97	5.44			110	504		35	8.13	4.30	5.56	* solid	
96	336		21	8.54	2.13	4.46	* solid	am	111	504		36	8.09	4.54	4.33	* solid	
97	336		22	8.37	2.51	4.69	* solid		112	504		37	7.99	4.86	5.68	* solid	
98	336		23	8.31	2.74	4.88	* solid		113	504		38	7.93	5.11	5.38	* solid	
99	336		24	8.32	2.97	5.14	* solid		114	504		39	7.85	5.40	5.36	* solid	
100	336		25	8.26	3.17	5.32	* solid		115	504		40	7.73	5.70	5.17	* solid	am

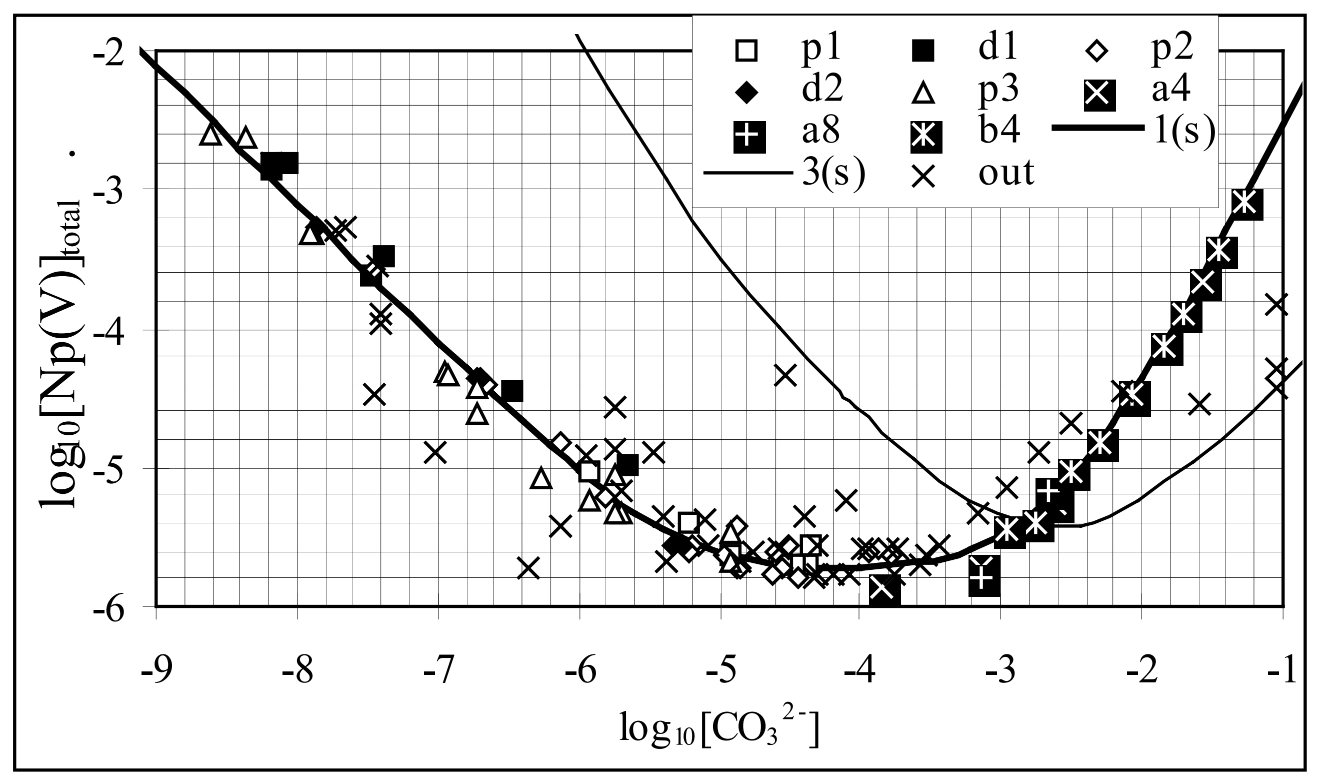
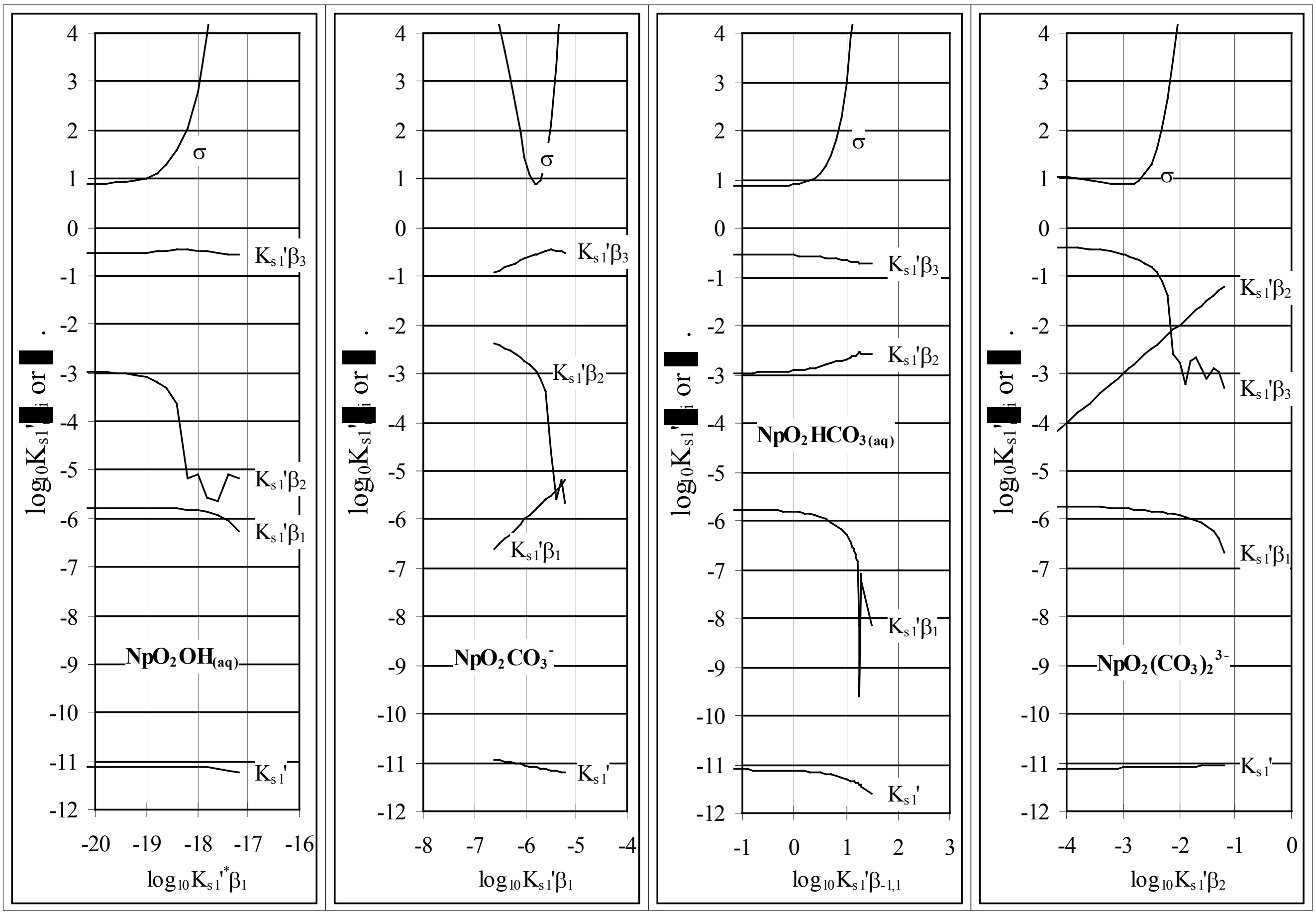
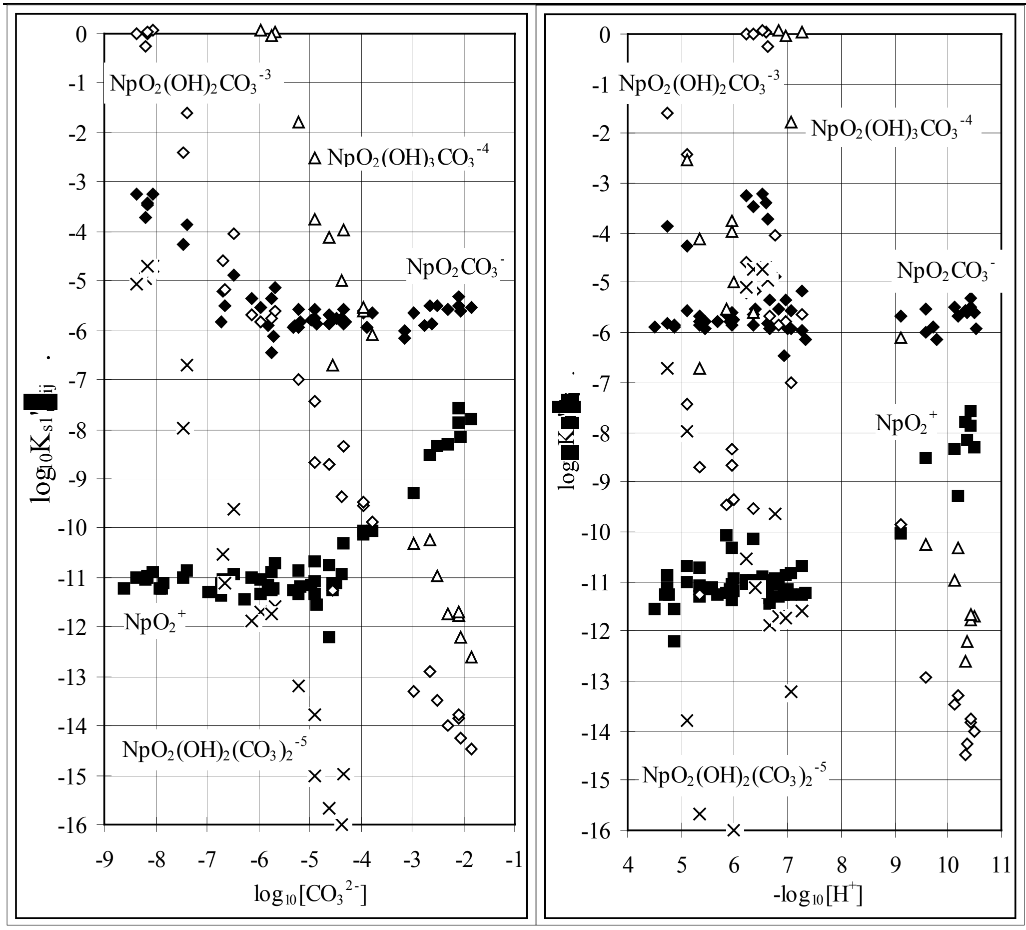
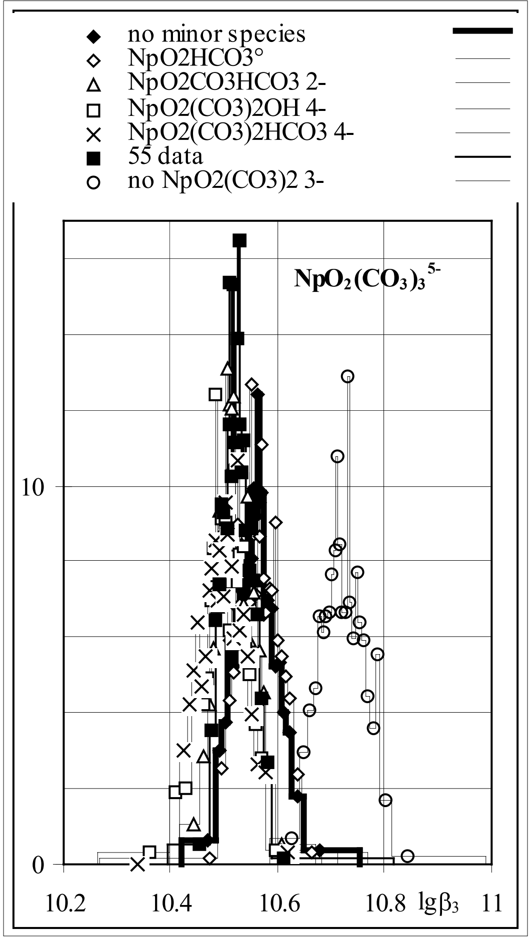


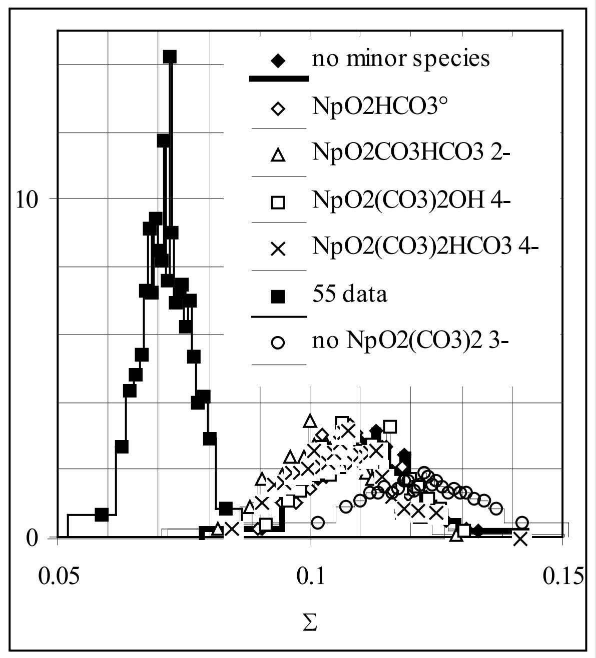
Figure: Np(V) solubility measured in carbonate media. The experimental points are from the above table (see its caption), "out" is for outlier. ai and bi are batches equilibrated 4 and 8 weeks (points 65 to 115 except the outliers). $NaNpO_2CO_{3(s)}$ "1s", and $Na_3NpO_2(CO_3)_{2(s)}$ "3s", solubility curves are calculated with the "[86GRE/ROB] and p.w" equilibrium constants tabulated above.





Figures: Sensitivity analysis. In 3 M $NaClO_4$ media. $K_{s1}' = Ks_1 / [Na^+] = [NpO_2^+] [CO_3^{2-}]$. Ks_1 is $NaNpO_2CO_{3(s)}$ solubility product. $\beta_i = ([NpO_2(CO_3)_i^{1-2i}] / [NpO_2^+] [CO_3^{2-}]^i)$. $\beta_{i,j} = [NpO_2(OH)_i(CO_3)_j^{1-2j-i}] [H^+]^i / ([NpO_2^+] [CO_3^{2-}]^j)$, $^*\beta_i = \beta_{i,0}$, $\beta_i = \beta_{0,i}$. Note that $\beta_{-1,1} = [NpO_2HCO_{3(aq)}] / ([NpO_2^+] [H^+] [CO_3^{2-}])$. Curve fitting results are plotted (previous page) as a function of the formation constant of one selected soluble species, its fitted value corresponds to the least square sum, σ^2, minimum. When hardly no minimum was found, the corresponding species cannot be detected and its formation constant cannot then be fitted, even when curve fitting programs give a number. In the figures above, an equilibrium constant is calculated from each experimental point assuming that all the other ones are constant (and equal to their fitting value): only when a constant value (within uncertainty) is found as a function of chemical conditions (namely $[CO_3^{2-}]$ and $[H^+]$), the corresponding equilibrium constant can be determined (mainly from the experimental measurements in these chemical conditions).





Figures: Statistical distribution of equilibrium constant values (also continued next page). Among the 55 (or more) experimental data, 55 (or more) have been chosen at random with repetitions. Curve fitting was then performed, and this was repeated 1000 times. Statistical analysis, and the histograms presented in these figures, were deduced from the 1000 set of equilibrium constants obtained with **this "bootstrap" algorithm** ([89CAC] Caceci M. *Estimating Error Limits in Parametric Curve Fitting*. Anal. Chem. 61, 20, 2324-2327 (1989)). We used the program written by Marco Caceci [89CAC]. Typical histograms are presented here.

$NaNpO_2CO_{3(s)}$ X-ray diffraction patterns.

Figure: Schematic X-ray diffraction patterns are plotted. *1* means $NaNpO_2CO_{3(s)}$, *2* means $Na_3NpO_2(CO_3)_{2(s)}$, *hyd.* means completely hydrated compound: the solid compound was sampled after solid equilibration with the solution that was used for solubility measurements and where this solubility usually showed that equilibrium was obtained. All the other compounds were prepared by precipitation and eventually heat treatment; but solid / liquid equilibrium was probably not obtained in any of them: Volkov and co-workers [77VOL/VIS, 79VOL/TOM, 79VOL/VIS and 81VOL/VIS] prepared and characterised the compounds, while Kim and co-workers [94MEI and 95NEC/RUN] measured their solubility (see the Appendix A); but it is not clear whether their $NaNpO_2CO_{3(s)}$ x-ray diffraction patterns were obtained before or after solubility equilibration. *1hyd.a (b, c or d)*, the letters correspond to the 1a, 1b, 1c and 1d compounds tabulated next page. For these compounds, intensities were visually estimated, theoretical patterns are plotted (calculated with the fitted lattice parameters tabulated next page) where extra lines are bolded, except the one at about 6.55 Å that is bolded to point out it is the strongest one (for this reason it is slightly broader than the other ones). For the other compounds thick lines (arbitrary thickness) correspond to diffuse lines, $Na_3NpO_2(CO_3)_{2(s)}$ spectra are darker only for presentation. For the [77VIS/VOL] spectra, intensities were visually estimated. For these spectra the authors proposed hydration numbers (3.5 to 0) from thermogravimetric studies: they were then obtained by increasing temperature from the $NaNpO_2CO_{3(s)}$,$3.5H_2O$ starting compounds. *?* corresponds to a compound that was assumed to be hydrated $Na_{0.6}NpO_2(CO_3)_{0.8(s)}$ by the authors; but heating it up to 350°C gave a compound with the same pattern as the $NaNpO_2CO_{3(s)}$ one obtained in the present work (*1hyd.a*). Note that [94MEI] probably also obtained it as an impurity. *??* corresponds to a compound that was assumed to be hydrated $Na_4NpO_2(CO_3)_{2.5(s)}$ by the authors; but this review considered from its x-ray diffraction pattern that it could as well have been $Na_3NpO_2(CO_3)_{2(s)}$. This figure was not shown at Migration'91, part of it was in European reports.

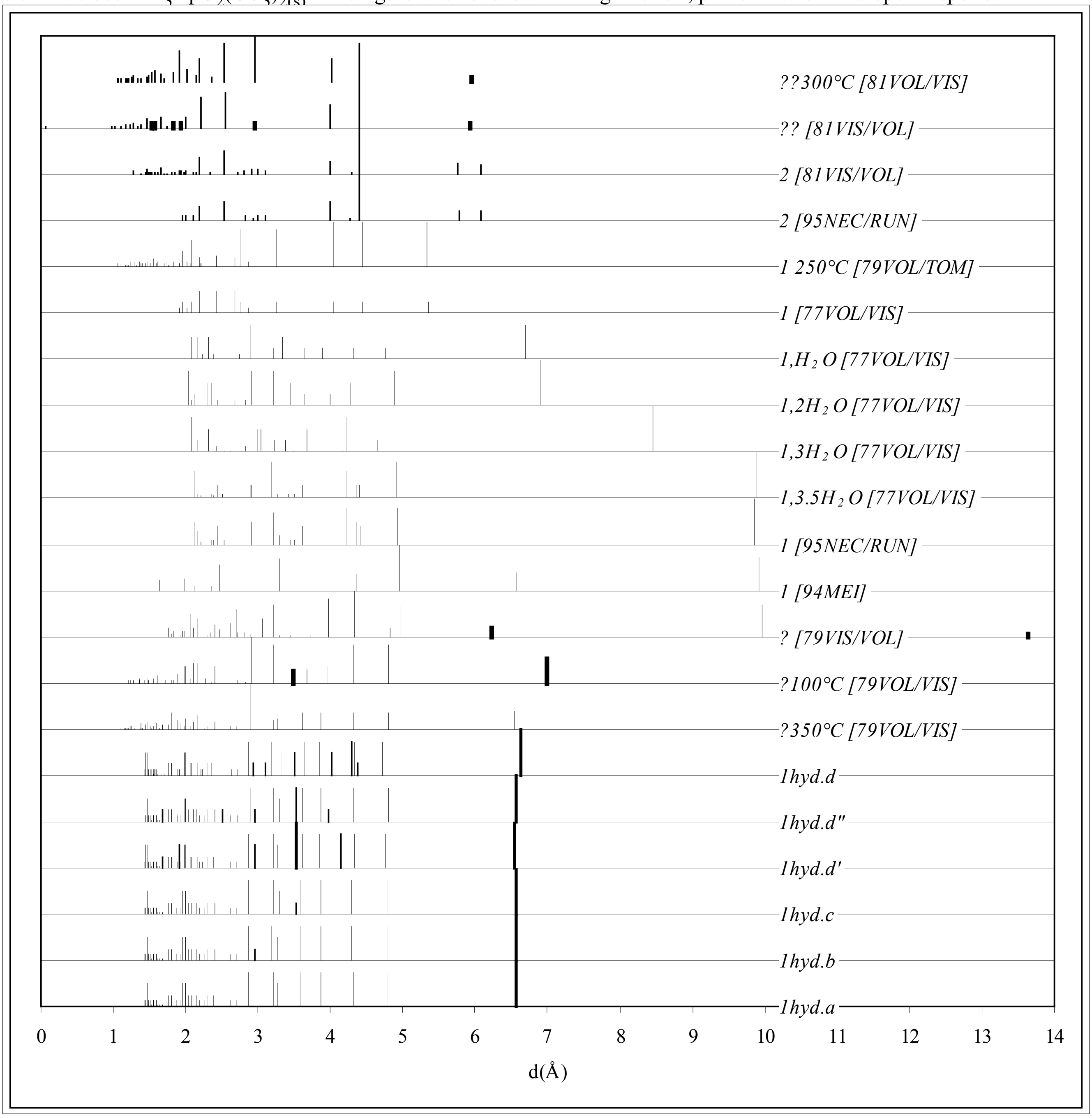


Table: Just before measuring solubility, the solution was filtered and the solid was let for drying at the air overnight (in the ventilated glove box). It was then sealed in glass capillary by *Jean Massé*, who registered the diffraction pattern. λ = 1.5405A. Intensities were estimated visually: very strong (S), strong (s), medium (s), weak (w), very weak (vw), and (l) for broad ones. The solid collected with point number n = 41 of the solubility result table, is named 1a, its lattice parameters are a = 4.784(2)A, b = 6.556(4)A, c = 4.316(3), and R = 0.0017 for 33 rays; they are fitted using Volkov et col. indexation [79VOL/VIS] of their heated (up to 350°C) "$Na_{0,6}NpO_2(CO_3)_{0,8(s)}$" compound whose diffraction pattern is significatively different from their other "$NaNpO_2CO_{3(s)},nH_2O$" compounds prepared at various temperatures [77VOL/VIS].

Intensity	hkl	observed 2 θ	calculated 2 θ	d(A)	Intensity	hkl	observed 2 θ	calculated 2 θ	d(A)
S(l)	010	13.52	13.49	6.5515		131	50.56	50.51	1.8043
s	100	18.46	18.53	4.7811	w	022	50.56	50.60	1.8013
s	001	20.55	20.56	4.3129	w	221	51.79	51.79	1.7625
s	110	23.04	22.99	3.8621		122		54.34	1.6856
s	011	24.66	24.67	3.6024		040		56.06	1.6380
m	020	27.14	27.18	3.2758		230		57.03	1.6124
s	101	27.83	27.81	3.2025		202	57.73	57.46	1.6013
s	111	30.99	31.03	2.8772	vw	300	57.73	57.76	1.5938
vw	120	33.00	33.10	2.7024		212	59.67	59.32	1.5555
vw	021	34.40	34.32	2.6087		140	59.67	59.57	1.5496
w	200	37.54	37.57	2.3906	vw	310	59.67	59.61	1.5486
w	121	39.32	39.28	2.2900		032		60.22	1.5345
vw	210	40.25	40.09	2.2458		041		60.36	1.5313
	030		41.28	2.1839	vw	231	61.33	61.28	1.5104
w	002	41.78	41.82	2.1565		301		61.98	1.4950
w	201	43.07	43.20	2.0909		132	63.67	63.58	1.4611
w	012	44.14	44.14	2.0484	m	141	63.67	63.72	1.4583
m	211	45.50	45.46	1.9919		311	63.67	63.76	1.4575
	130	45.50	45.60	1.9865		222	65.00	64.70	1.4387
	102	45.50	46.10	1.9658		003	65.00	64.74	1.4377
vw	220	47.05	46.98	1.9311	vw	320	65.00	64.97	1.4332
	112		48.26	1.8829					

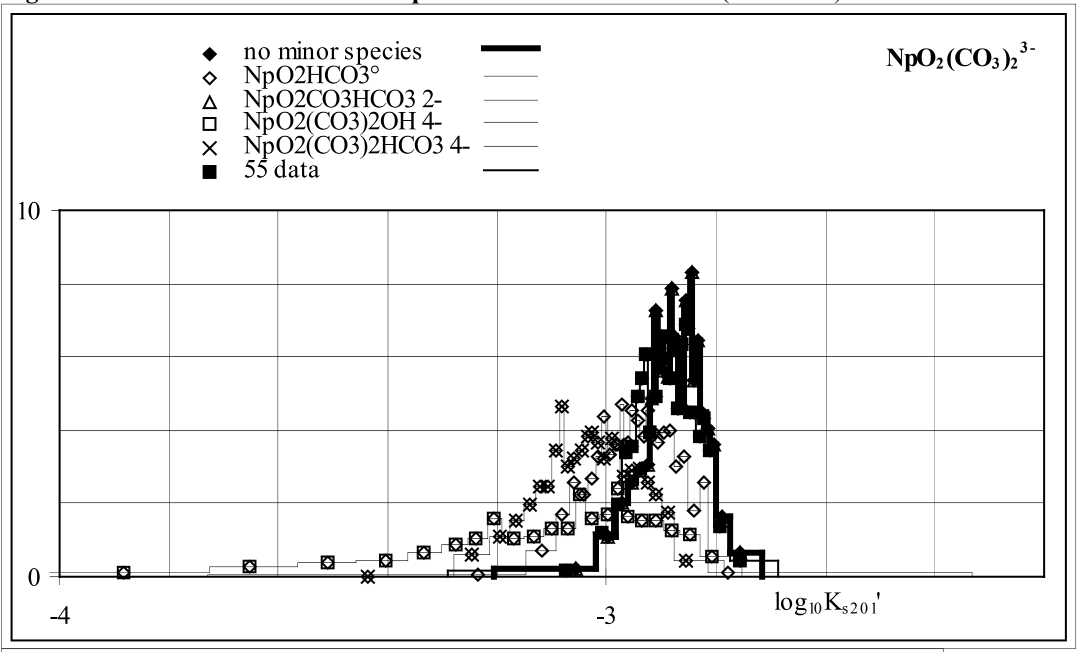
n is the sample number of the solubility result table, a, b and c (Ä) are the lattice fitted parameters (and uncertainties), R1 and R2 the standard deviation computed for the main rays or all of them respectively (and the number of rays used), *low intensity supplementary rays, **supplementary rays with at least medium intensity and many other ones.

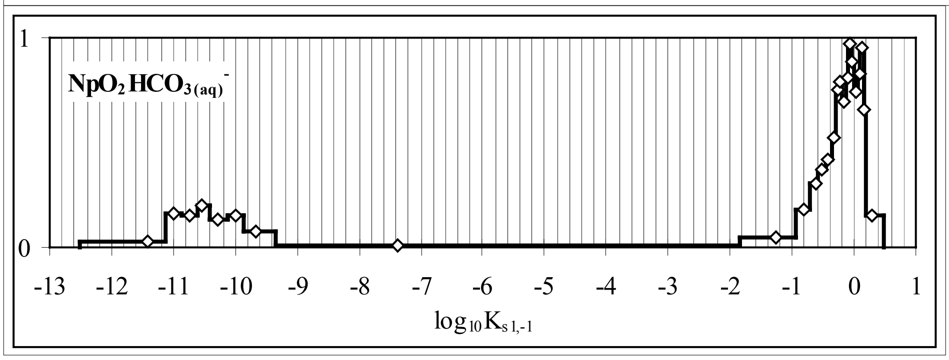
n	name		a	b	c	R1	R2
41	1a		4.784(2)	6.556(4)	4.316(3)	0.0015(27)	0.0017(33)
51	1a		4.779(3)	6.555(4)	4.304(2)	0.0017(22)	0.0024(35)
23	1b	*	4.760(3)	6.573(6)	4.325(2)	0.0013(20)	0.0013(20)
33	1b	*	4.786(3)	6.559(3)	4.295(2)	0.0012(26)	0.0017(34)
30	1c	*	4.788(3)	6.568(4)	4.299(3)	0.0021(25)	0.0026(35)
22	1d	**	4.768(5)	6.544(7)	4.327(3)	0.0016(15)	0.0022(23)
38	1d	**	4.791(2)	6.571(4)	4.312(2)	0.0016(16)	0.0016(33)
	1d	**	4.720(3)	6.622(7)	4.329(3)	0.0011(16)	0.0016(22)

This presentation (below) of the supplementary rays shows the names given to the solid compounds (that might contain mixtures of unstable phases).

name	1b *	1b *	1c *	1d **	1d **	1d **	name	1b *	1b *	1c *	1d **	1d **	1d **
2θ\ n	23	33	30	22	38		2θ\ n	23	33	30	22	38	
20.255						w	30.225	w	w		m	w	
20.645						s	30.555						w
21.405				s			35.860					w	
22.105						m	37.050						
22.390					w		43.295						
25.17					s		47.605				m		
25.275			w	S			54.650					w	
25.325						m	54.765				w		
28.805						w							

Figures: Statistical distribution of equilibrium constant values. (continued)





Np(V) spectrophotometry in carbonate hydroxide media.

This work was performed by *Laure Gorgeon* for a pre Ph-D stage (DEA). The initial Np(V) solution compositions are above each block of table. Non indicated concentration unit is M (mole/l). Small volumes of concentrated reactant, R (= NaOH, either Na_2CO_3 or Np(V)) solutions are added directly into the 22 ml, 10 cm path length cuvette. The slope is $\log_{10}(A_t/[Np(V)]_t)$ vs. $\log_{10}[R]$ linear regression.

$[Na_2CO_3]$ 0.1, $[NaClO_4]$ 2.8 slope 1.23

NaOH 9.9 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0		1.027		
0.10	0.04	-1.35	1.022	0.088	1.93
0.20	0.09	-1.05	1.018	0.384	2.58
0.30	0.13	-0.88	1.013	0.544	2.73
0.40	0.18	-0.75	1.009	0.688	2.83
0.50	0.22	-0.66	1.004	0.760	2.88
0.60	0.26	-0.58	1.000	0.788	2.90
0.70	0.31	-0.52	0.995		

$[Na_2CO_3]$ 0.5, $[NaClO_4]$ 2 slope 0.69

NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00		0.1027		
0.10	0.04	-1.35	0.1022		
0.20	0.09	-1.05	0.1018	0.0184	2.26
0.30	0.13	-0.88	0.1013	0.0256	2.40
0.55	0.24	-0.62	0.1002	0.0452	2.65
0.80	0.34	-0.46	0.0991	0.0536	2.73
1.30	0.55	-0.26	0.0970	0.0664	2.84
1.80	0.74	-0.13	0.0949	0.0736	2.89

$[Na_2CO_3]$ 0.98 slope 0.66

NaOH 9.9 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0		1.027		
0.20	0.09	-1.05	1.018		
0.40	0.18	-0.75	1.009	0.2	2.30
0.60	0.26	-0.58	1.000	0.34	2.53
0.80	0.35	-0.46	0.991	0.42	2.63
1.00	0.43	-0.37	0.982	0.524	2.73
1.20	0.51	-0.29	0.974	0.556	2.76
1.40	0.59	-0.23	0.966	0.58	2.78
1.60	0.67	-0.17	0.957	0.616	2.81
1.80	0.75	-0.13	0.949	0.628	2.82
2.00	0.83	-0.08	0.941	0.648	2.84
2.20	0.90	-0.05	0.934	0.676	2.86
3.20	1.26	0.10	0.897	0.68	2.88

$[Na_2CO_3]$ 1.5 slope 0.90

NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00		0.1027		
0.25	0.11	-0.96	0.1015		
0.50	0.22	-0.66	0.1004	0.0184	2.26
0.75	0.32	-0.49	0.0993	0.0304	2.49
1.00	0.43	-0.37	0.0982	0.0368	2.57
1.25	0.53	-0.28	0.0972	0.0424	2.64
1.50	0.63	-0.20	0.0961	0.0504	2.72
1.75	0.72	-0.14	0.0951	0.0512	2.73

$[Na_2CO_3]$ 0.49 slope 0.52

NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0		1.027		
0.10	0.04	-1.35	1.022	0.100	1.99
0.20	0.09	-1.05	1.018	0.220	2.33
0.30	0.13	-0.88	1.013	0.296	2.47
0.40	0.18	-0.76	1.009	0.360	2.55
0.50	0.22	-0.66	1.004	0.404	2.60
0.60	0.26	-0.58	1.000	0.436	2.64
0.70	0.30	-0.52	0.995	0.456	2.66
0.80	0.34	-0.46	0.991	0.486	2.69
0.90	0.39	-0.41	0.987	0.492	2.70
1.00	0.43	-0.37	0.982	0.498	2.70
1.25	0.53	-0.28	0.972	0.536	2.74
1.50	0.63	-0.20	0.961	0.540	2.75
1.75	0.72	-0.14	0.951	0.544	2.76
2.00	0.82	-0.09	0.941	0.540	2.76
2.50	1.00	0.00	0.922	0.540	2.77

$[Na_2CO_3]$ 0.49, $[NaClO_4]$ 2 slope 0.86

NaOH 9.9 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00	0.00	1.009	0.00	
0.10	0.04	-1.35	1.004	0.00	
0.20	0.09	-1.05	1.000	0.07	1.83
0.30	0.13	-0.88	0.995	0.19	2.27
0.40	0.18	-0.75	0.991	0.27	2.43
0.50	0.22	-0.66	0.987	0.34	2.54
0.60	0.26	-0.58	0.982	0.40	2.61
0.70	0.31	-0.52	0.978	0.44	2.65
0.80	0.35	-0.46	0.974	0.50	2.71
1.00	0.43	-0.37	0.965	0.58	2.78
1.20	0.51	-0.29	0.957	0.68	2.85
1.40	0.59	-0.23	0.949	0.70	2.87
1.90	0.79	-0.10	0.929	0.74	2.90
2.40	0.97	-0.01	0.910	0.75	2.91
2.90	1.15	0.06	0.891	0.72	2.90

$[Na_2CO_3]$ 1, $[NaClO_4]$ 1 slope 0.99

NaOH 9.8 M (ml)	x = [OH]	lg x	$[Np]_t$ (mM)	absorb. A	y = $A/[Np]_t$ lg y
0.00	0.00		1.027		
0.10	0.04	-1.35	1.022		
0.20	0.09	-1.05	1.018	0.076	1.87
0.30	0.13	-0.88	1.013	0.124	2.09
0.40	0.18	-0.76	1.009	0.144	2.15
0.50	0.22	-0.66	1.004	0.212	2.32
0.70	0.30	-0.52	0.995	0.316	2.50
0.90	0.39	-0.41	0.987	0.348	2.55
1.10	0.47	-0.33	0.978	0.428	2.64
1.30	0.55	-0.26	0.970	0.472	2.69
1.50	0.63	-0.20	0.961	0.52	2.73
1.70	0.70	-0.15	0.953	0.536	2.75

$[Na_2CO_3]$ 0.5, $[NaClO_4]$ 2 [NaOH] 0.43					slope	0.26
Na_2CO_3	x =		absorb.	y = $A/[Np]_t$		
(ml)	$[CO_3]$	lg x	A	y	[OH]	lg[OH]
	0.2940	-0.53	0.086	837.39	1.20	0.08
15.00	0.1764	-0.75	0.078	759.49	1.32	0.12
10.00	0.1176	-0.93	0.072	701.07	1.38	0.14
9.00	0.1058	-0.98	0.068	662.12	1.39	0.14
8.00	0.0940	-1.03	0.064	623.17	1.40	0.15
5.00	0.0588	-1.23	0.048	467.38	1.44	0.16
3.00	0.0350	-1.46	0.038	370.01	1.46	0.16
1.70	0.0200	-1.70	0.030	292.11	1.48	0.17
	1.0000	0.00	0.074	720.55	0.50	-0.30

$[Na_2CO_3]$ 0.498, $NaClO_4]$ 2 [NaOH] 0.4				slope 0.09
Np 10.27mM	x= $[Np]_t$		absorb.	y = $A/[Np]_t$
(ml)	(mM)	lg x	A	lg y
0.00	0.1027	-3.99	0.04	2.61
0.10	0.1492	-3.83	0.05	2.56
0.20	0.1952	-3.71	0.07	2.58
0.30	0.2409	-3.62	0.09	2.57
0.40	0.2861	-3.54	0.10	2.56
0.60	0.3754	-3.43	0.13	2.53
0.80	0.4631	-3.33	0.16	2.55
1.00	0.5492	-3.26	0.21	2.58
1.20	0.6339	-3.20	0.27	2.62
1.40	0.7171	-3.14	0.30	2.62
1.60	0.7990	-3.10	0.34	2.63
1.80	0.8794	-3.06	0.39	2.65
2.00	0.9585	-3.02	0.44	2.66
2.20	1.0363	-2.98	0.49	2.67

$[Na_2CO_3]$ 1.47				slope	0.95
NaOH 9.9 M	x =		$[Np]_t$	absorb.	y = $A/[Np]_t$
(ml)	[OH]	lg x	(mM)	A	lg y
0			1.027		
0.25	0.11	-0.95	1.015	0.04	1.60
0.50	0.22	-0.66	1.004	0.20	2.31
0.75	0.33	-0.49	0.993	0.28	2.44
1.00	0.43	-0.37	0.982	0.36	2.56
1.25	0.53	-0.27	0.972	0.42	2.63
1.50	0.63	-0.20	0.961	0.47	2.69
1.75	0.73	-0.14	0.951	0.51	2.73
2.00	0.83	-0.08	0.941	0.51	2.73
2.25	0.92	-0.04	0.932	0.56	2.78
2.50	1.01	0.00	0.922	0.56	2.78
2.75	1.10	0.04	0.913	0.58	2.81
3.00	1.19	0.07	0.904	0.58	2.81
3.25	1.27	0.11	0.895	0.60	2.83
4.25	1.60	0.20	0.861	0.59	2.84

$[Na_2CO_3]$ 1.497, [NaOH] 0.515				slope 0.01
Np 10.27mM	x= $[Np]_t$		absorb	y = $A/[Np]_t$
(ml)	(mM)	lg x	A	lg y
0	0.1027	-4.0	0.048	2.67
0.1	0.1492	-3.8	0.064	2.63
0.2	0.1952	-3.7	0.069	2.55
0.3	0.2409	-3.6	0.100	2.62
0.4	0.2861	-3.5	0.120	2.62
0.5	0.3309	-3.5	0.147	2.65
0.7	0.4194	-3.4	0.180	2.63
0.9	0.5063	-3.3	0.228	2.65

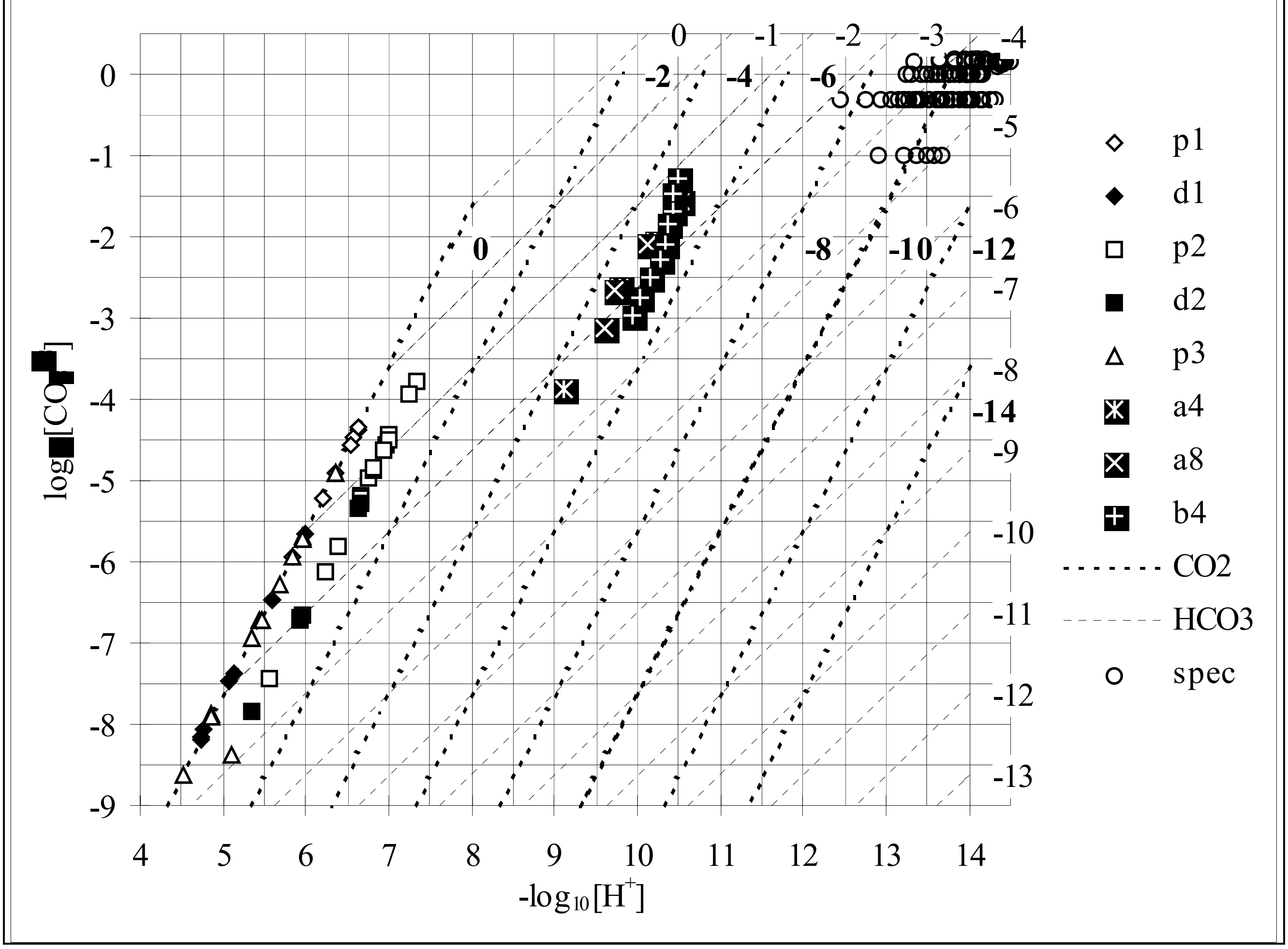
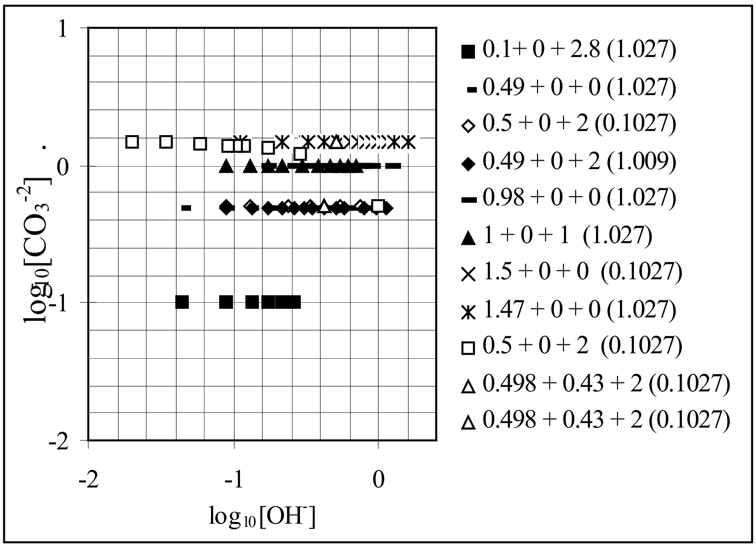


Figure: Experimental conditions of solubility and spectrophotometric measurements in 3 M $NaClO_4$ aqueous solutions. pi and di are respectively the ith precipitation and dissolution. ai and bi are batches equilibrated i weeks. spec are spectrophotometric measurements CO2 and HCO3 lines are respectively constant $[CO_2]$ and $[HCO_3^-]$ corresponding to $\log_{10}[P_{CO2}]$ and $\log_{10}[HCO_3^-]$ values written on the figure



Experimental conditions of spectrophotometric measurement. The numbers on the figure correspond to the initial Na_2CO_3, $NaClO_4$, NaOH and Np(V) concentrations used to prepare the aqueous solutions for spectrophotometric measurements as tabulated above.

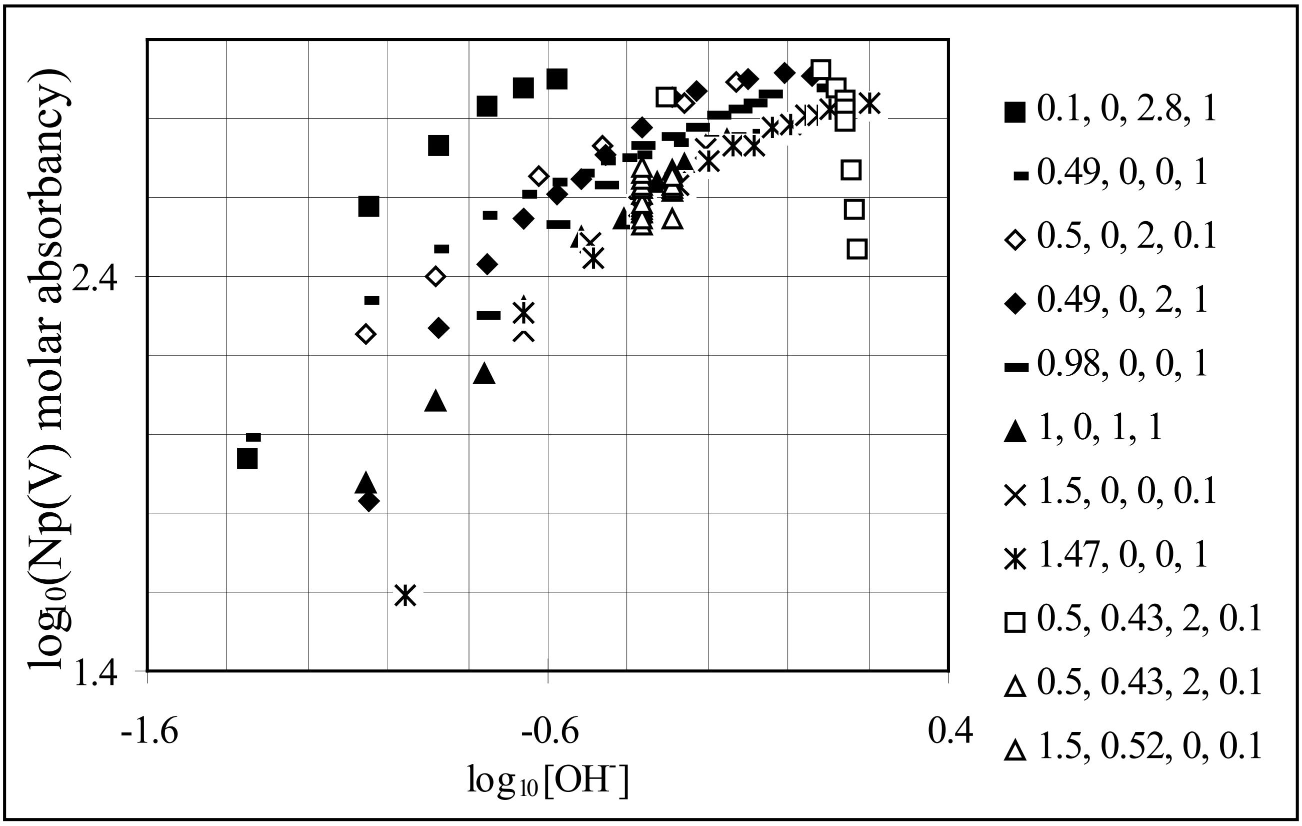
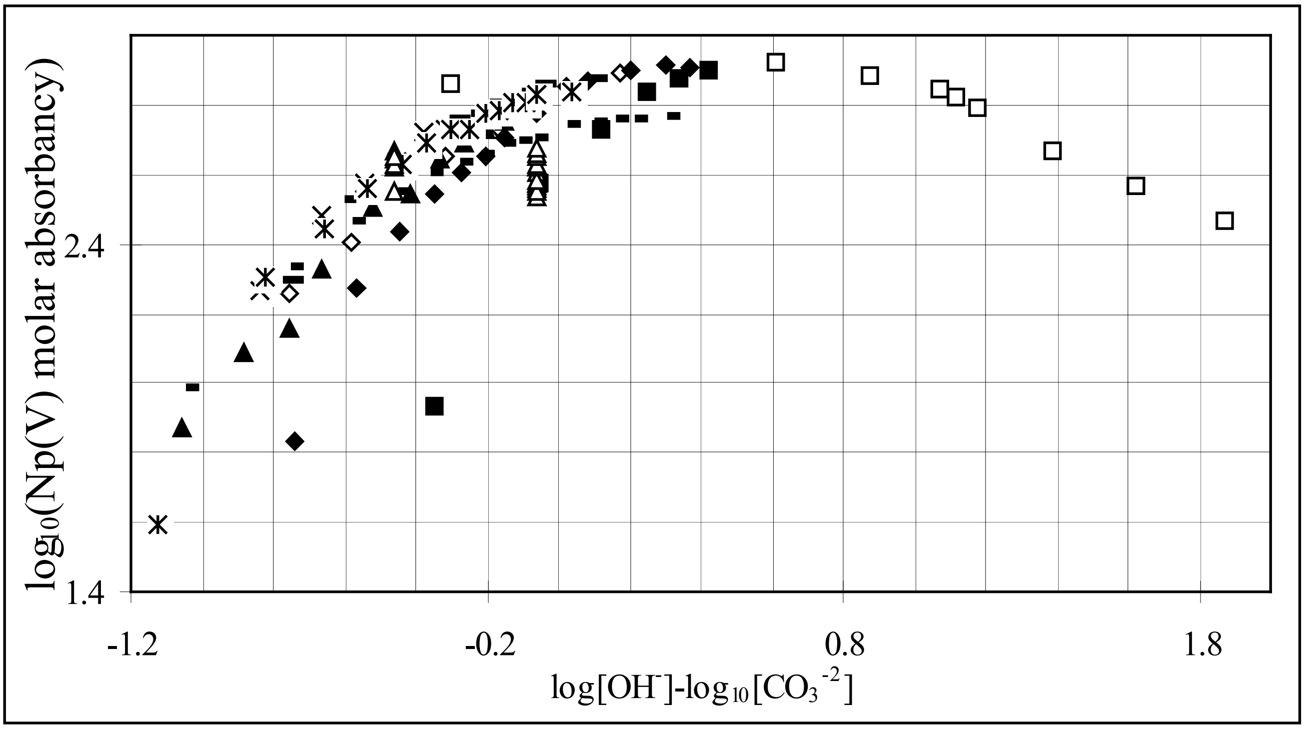
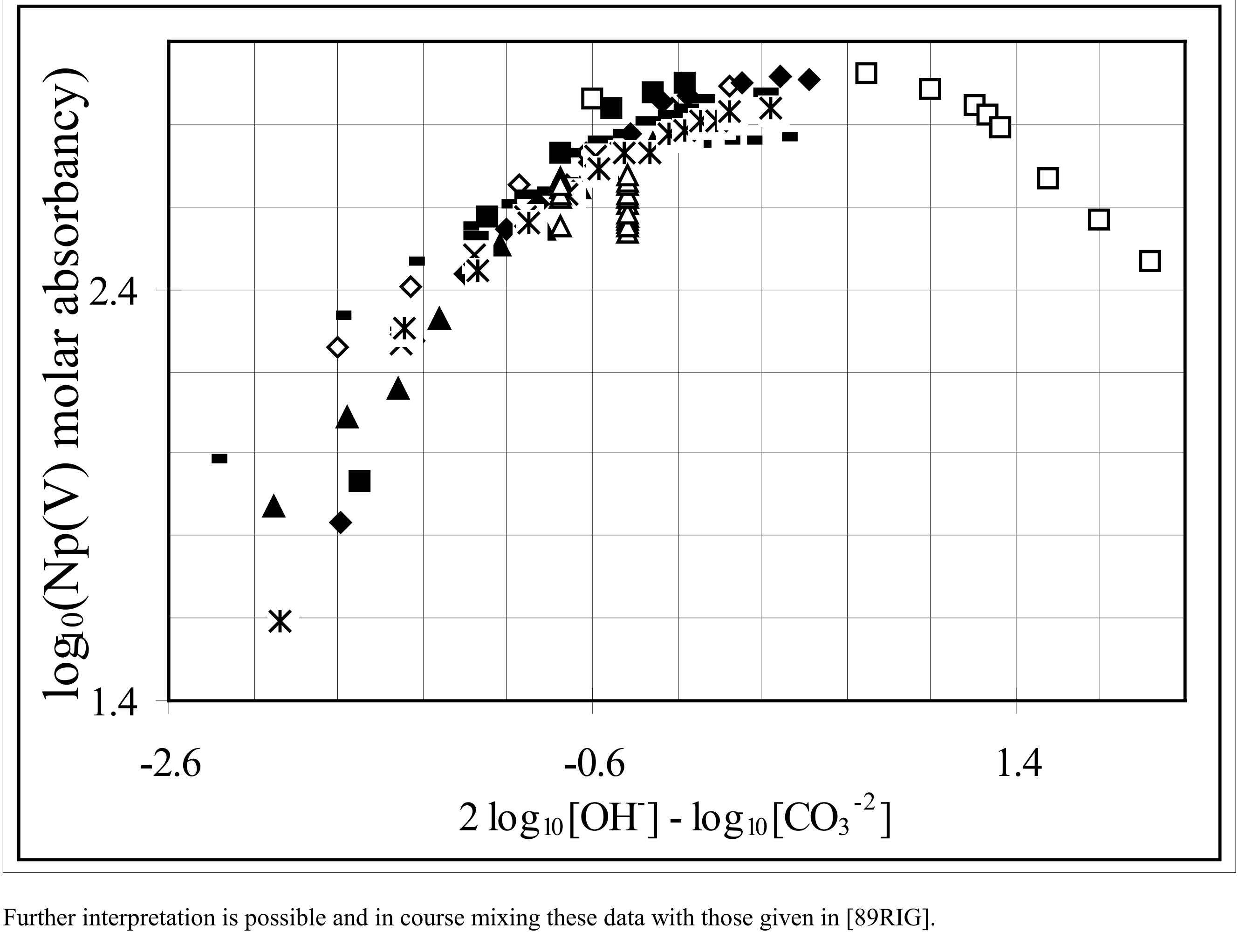


Figure: Np(V) spectrophotometric study. The data tabulated above are plotted on this figures. The numbers on the figure have the same meaning as in the above one. The data do not depend on$[Np(V)]_t$, and are less scattered when plotted as a function of $2 \log_{10}[OH^-] - \log_{10}[CO_3^{-2}]$ which indicates the limiting complex, $NpO_2(CO_3)_3^{-5}$, mainly dissociates according to the reaction:

$NpO_2(CO_3)_3^{-5} + 2\ OH^- \Leftrightarrow NpO_2(OH)_2(CO_3)_2^{-5} + CO_3^{-2}$.





Further interpretation is possible and in course mixing these data with those given in [89RIG].

Uncertainty is 1.96 standard deviation. Italicised numbers are unbelievable values.

[66GOR/ZEN]

Experimental data reported in this publication.

	mol./l	(mg/l)		Calculated by this review				
K_2CO_3	$[K_2CO_3]$	[Np(V)]		$\log_{10}$[Np(V)]	$\log_{10}[K^+]$	$\log_{10}[CO_3^{-2}]$	$\log_{10}K_{s2,3}$	$\log_{10}K_{s1,3}$
	0	10.3		-4.36				
	0.2	23		-4.01	-0.40	-0.70		-3.01
50%	5.573	38		-3.79	1.05	0.75	-1.40	
50%	5.573	840	mother-liquor	-2.45	1.05	0.75	-0.06	
	0.2	103	wash solution	-3.36	-0.40	-0.70		-2.36

Cs_2CO_3	$[Cs_2CO_3]$	[Np(V)]		$\log_{10}$[Np(V)]	$\log_{10}[Cs^+]$	$\log_{10}[CO_3^{-2}]$	$\log_{10}K_{s2,3}$	$\log_{10}K_{s1,3}$
	0	22.7		-4.02				
	0.2	87.5		-3.43	-0.40	-0.70		-2.43
50%	5.573	492		-2.68	1.05	0.75	-0.29	
50%	5.573	1751.1	mother-liquor	-2.13	1.05	0.75	0.26	
	0.2	95	wash solution	-3.40	-0.40	-0.70		-2.40

[71MOS5]

Experimental data from tables of the [71MOS5] publication. c = $[(NH_4)_2CO_3]$, sX and SX are Np measured solubility, where the initial solid phase was $Np(OH)_{4(s)}$ for s4, $NH_4NpO_2CO_{3(s)}$ for S5, $NpO_2OH_{(s)}$ for s5, $NpO_2(OH)_{2s}$ for s6, $(NH_4)_4NpO_2(CO_3)_{3s}$ for S6.

c	s4	pH	S5	pH	s5	pH	s6	pH	S6	pH
0	0.00617	8.6	0.00001	8.8	7.94E-06	8.6	0.000794	8.8	0.106	8.5
0.1							0.00329	8.8	0.0654	8.55
0.15	0.00692	8.6					0.00667	8.82		
0.2			1.51E-05	8.8	1.17E-05	8.6	0.0144	8.85		
0.25							0.0184	8.9		
0.3							0.0193	8.95		
0.45							0.0214	9		
0.5					1.69E-05	8.6			0.0226	8.6
0.6	0.00891	8.65	4.51E-05	8.8			0.0212	9.05		
0.75					5.51E-05	8.7	0.0156	9.07	0.016	8.7
1	0.0132	8.7	0.000062	8.9	0.000087	8.75	0.0133	9.1	0.0127	8.8
1.25			0.0001	8.9	0.000178	8.8	0.00823	9.1	0.00886	8.9
1.5	0.0174	8.7	0.000123	9	0.000266	8.8			0.00831	8.95
1.8	0.019	8.75			0.000355	8.85			0.0665	9.05
2			0.000105	9	0.000229	8.9				
2.2	0.0219	8.8	7.81E-05	9	0.000106	9			0.00451	9.1

Speciation calculated by this review. The stability constant, $K_{s1,3} = [NH_4^+]\,[NpO_2(CO_3)_3^{-5}] / [CO_3^{-2}]^2$ was calculated from the S5 solubility value (previous table) assuming that only the limiting complex, $NpO_2(CO_3)_3^{-5}$, was formed, while $k_{s1,3}$ was calculated with the s5 value.

c	lg p	$lg[NH_4^+]$	$lg[NH_3]$	$lg[OH^-]$	$lg[CO_3^{-2}]$	$lg[HCO3^-]$	lgP_{CO2}	$-lg[H^+]$	$lgK_{s1,3}$	$lgk_{s1,3}$
0.1	0.0012	-0.938	-1.073	-4.657	-1.809	-1.074	-2.609	9.238		
0.15	0.0017	-0.755	-0.906	-4.644	-1.587	-0.907	-2.462	9.241		
0.2	0.0023	-0.625	-0.788	-4.636	-1.429	-0.789	-2.359	9.244	-2.59	-2.70
0.25	0.0029	-0.524	-0.697	-4.632	-1.306	-0.698	-2.279	9.245		
0.3	0.0035	-0.441	-0.623	-4.630	-1.207	-0.624	-2.214	9.247		
0.45	0.0052	-0.257	-0.460	-4.632	-0.985	-0.461	-2.070	9.250		
0.5	0.0058	-0.209	-0.418	-4.634	-0.928	-0.418	-2.033	9.251		-3.13
0.6	0.0070	-0.126	-0.345	-4.640	-0.829	-0.345	-1.969	9.254	-2.81	
0.75	0.0088	-0.025	-0.256	-4.652	-0.709	-0.256	-1.891	9.257		-2.87
1	0.0118	0.107	-0.142	-4.676	-0.555	-0.142	-1.791	9.262	-2.99	-2.84
1.25	0.0149	0.208	-0.053	-4.704	-0.436	-0.054	-1.714	9.268	-2.92	-2.70
1.5	0.0180	0.292	0.018	-4.735	-0.339	0.018	-1.652	9.274	-2.94	-2.61
1.8	0.0218	0.375	0.089	-4.775	-0.242	0.089	-1.590	9.282		-2.59
2	0.0243	0.423	0.130	-4.803	-0.187	0.130	-1.556	9.288		
2.2	0.0269	0.467	0.167	-4.832	-0.136	0.167	-1.525	9.293		

Curve fitting results. $K_{s1,3} = [NH_4^+]\,[NpO_2(CO_3)_3^{-5}] / [CO_3^{-2}]^2$. $\log_{10}k_3 = -0.87$ were fixed.
$k_3 = [NpO_2(CO_3)_3^{-5}] / [NpO_2(CO_3)_2^{-3}] / [CO_3^{-2}]$. $\varepsilon_i = \varepsilon(NpO_2(CO_3)_i^{1-2i},NH_4^+)$

ε_3	ε_2	$\log_{10}K_{s1,3}$	±	± / $\pm_{min}$		ε_3	ε_2	$\log_{10}K_{s1,3}$	±	± / $\pm_{min}$
1.8	-0.16	-5.92	0.14615			0.6	-0.165	-6.273	0.273	1.997
2	-0.164	-5.907	0.138	1.010		0.5	0.035	-6.288	0.312	2.282
1.8	-0.176	-5.932	0.137	1.000		0.4	0.026	-6.410	0.405	2.966
1.5	-0.201	-5.986	0.140	1.025		0.25	-0.104	-6.622	0.626	4.586
1.25	-0.225	-6.048	0.152	1.113		0	-0.345	-6.981	1.057	7.736
1	-0.246	-6.129	0.179	1.308		0.6	1.488	-6.010	0.366	2.679
0.75	-0.238	-6.224	0.229	1.673		0.6	0.150	-6.140	0.312	2.283

[74SIM/VOL]

Solubility measurements. Concentration is in mol.l^{-1}. lg is $\log_{10}P_{CO2}$ is in atm. Potentiometric titrations

$[K_2CO_3]$	[Np]	°C	lg[Np]	$lg[K_2CO_3]$	$lgK_{s2,3}$	$pH_{1/2}$	[Np]?	$[K^+]$?	P_{CO2}	lg[Np]	lgP_{CO2}	$lg[CO_3^{-2}]$	lgK_{s3}	lgK_{s1}
1.2	8	20	-4.47	0.08	-3.41	4.8	0.03	0.09	1	-1.52	0	-7.9	-20.46	
1.2	17	80	-4.14	0.08	-3.08	5.2	0.03	0.03	1	-1.52	0	-7.1		-10.15

[74VIS/VOL]

Solubility reported in this publication.

mol.l^{-1} $[K_2CO_3]$	mg/l Np(V)	°C t	molar $\log_{10}[Np]$	molar $\log_{10}[CO_3^{-2}]$	molar $\log_{10}K_{s2,3}$	molar $lnK_{s2,3}$	kJ/mol. $\Delta G_{s2,3}$	J/mol./K $\Delta S_{s2,3}$	kJ/mol. $\Delta H_{s2,3}$
1.2	8	20	-4.47	0.08	-3.41	-7.85	19.14	-28.4	10.67[a]
1.2	17	80	-4.14	0.08	-3.08	-7.10	20.844		10.81[b]
				mean	-3.24	-7.48	18.53		
				±	0.5	1.15	2.85	67.27	20.26
		25					19.14		

$\log_{10}K_{s2,3} = \log_{10}[Np] + 3\log_{10}[K^+] - \log_{10}[CO_3^{-2}]$

$lnK_{s2,3} = 2.302585 \log_{10}K_{s2,3}$, $\Delta G_{s2,3} = -R/1000\ (0.008315)*T*lnK_{s2,3}$, $R = 8.314511$

$\Delta S_{s2,3} = -1000\ d\Delta G_{s2,3}/dt = -1000(\Delta G_{s2,3}(80) - \Delta G_{s2,3}(20))/(80 - 20)$

$\Delta H_{s2,3} =^{a} \Delta G_{s2,3}(25) + 298.15\ \Delta S_{s2,3} / 1000 =^{b} -R/1000\ d(lnK_{s2,3})/d(1/T)$

Potentiometric titration	$pH_{1/2}$	Np (mol.l^{-1})	K (mol.l^{-1})	P_{CO2}	$\log_{10}[CO_3^{-2}]$	$\log_{10}K_{s2}$	$\log_{10}K_{s1}$
$K_3NpO_2(CO_3)_{2(s)}$?	4.8	0.03?	0.09	1?	-7.9	*-20.46*	-10.47
$KNpO_2CO_{3(s)}$?	5.2	0.03?	0.03	1?	-7.1		-10.15
						mean	-10.31
						+/-	0.16

[75SAI/UEN]

Experimental data scanned by this review from the figure of the [75SAI/UEN] publication. M is Na_2CO_3 molarity (mol./l), m its molality (mol./kg). $\log_{10}K_{s2,3}$ was calculated by this review from the scanned experimental data.

M	$\log_{10}[Np]$	$\log_{10}m$	$\log_{10}[OH^-]$	$\log_{10}[CO_3^{-2}]$	M	$\log_{10}[Np]$	$\log_{10}m$	$\log_{10}[OH^-]$	$\log_{10}[CO_3^{-2}]$
1.6	-1.793	0.214	-3.656	0.183	0.2	-3.069	-0.697	-3.792	-0.797
1.2	-1.796	0.087	-3.633	0.052	0.15	-3.613	-0.823	-3.842	-0.942
0.6	-2.013	-0.218	-3.651	-0.269	0.1	-3.928	-1.000	-3.920	-1.153
0.4	-2.491	-0.395	-3.692	-0.460	0.07	-4.100	-1.154	-3.994	-1.344
0.3	-2.690	-0.521	-3.729	-0.598	0.05	-4.162	-1.300	-4.070	-1.532

$[Na_2CO_3]$ (mol.l^{-1})	0.4	0.3	0.2	0.15	0.1	0.07
$\log_{10}K_{s2,3}$	-1.72 ± 0.39	-1.78 ± 0.42	-1.97 ± 0.51	-2.57 ± 0.64	-2.91 ± 0.92	-3.03 ± 1.25

[77SAI/UEN]

Np(V) solubility from the figure 4 of this publication. $1/6\ A_8(NpO_2)_6(CO_3)_{21(s)} + 1/2\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_3^{-5} + 4/3\ A^{+3}$? where $A = Co(NH_3)_6^{+3}$. Linear regressions: $\log_{10}[Np] = -3.263 \pm 0.058 + (2.684 \pm 0.268) \log_{10}[Na_2CO_3]$ for $[ACl_3] = 0.04$ mol.l^{-1}$\log_{10}[Np] = -4.701 \pm 0.272 + (-0.603 \pm 0.197) \log_{10}[ACl_3]$ for $[Na_2CO_3] = 0.5$ mol.l^{-1}.

mol./l $[Na_2CO_3]$	mol./l $[ACl_3]$	lg(mg/ml) lg Np	molar $lg[Na_2CO_3]$	molar lg[Np]	mol./l $[Na_2CO_3]$	mol./l $[ACl_3]$	lg(mg/ml) lg Np	molar $lg[Na_2CO_3]$	molar lg[Np]
0.5	0.04	-1.65	-0.301	-4.025	0.5	0.01	-0.99	-0.301	-3.365
0.75	0.04	-1.2	-0.125	-3.575	0.5	0.02	-1.43	-0.301	-3.805
1	0.04	-0.95	0	-3.325	0.5	0.04	-1.57	-0.301	-3.945
1.35	0.04	-0.65	0.130	-3.025	0.5	0.06	-1.62	-0.301	-3.995
1.6	0.04	-0.36	0.204	-2.735	0.5	0.08	-1.61	-0.301	-3.985
1.85	0.04	-0.13	0.267	-2.505	0.5	0.1	-1.7	-0.301	-4.075
2	0.04	0	0.301	-2.375	0.5	0.12	-1.73	-0.301	-4.105

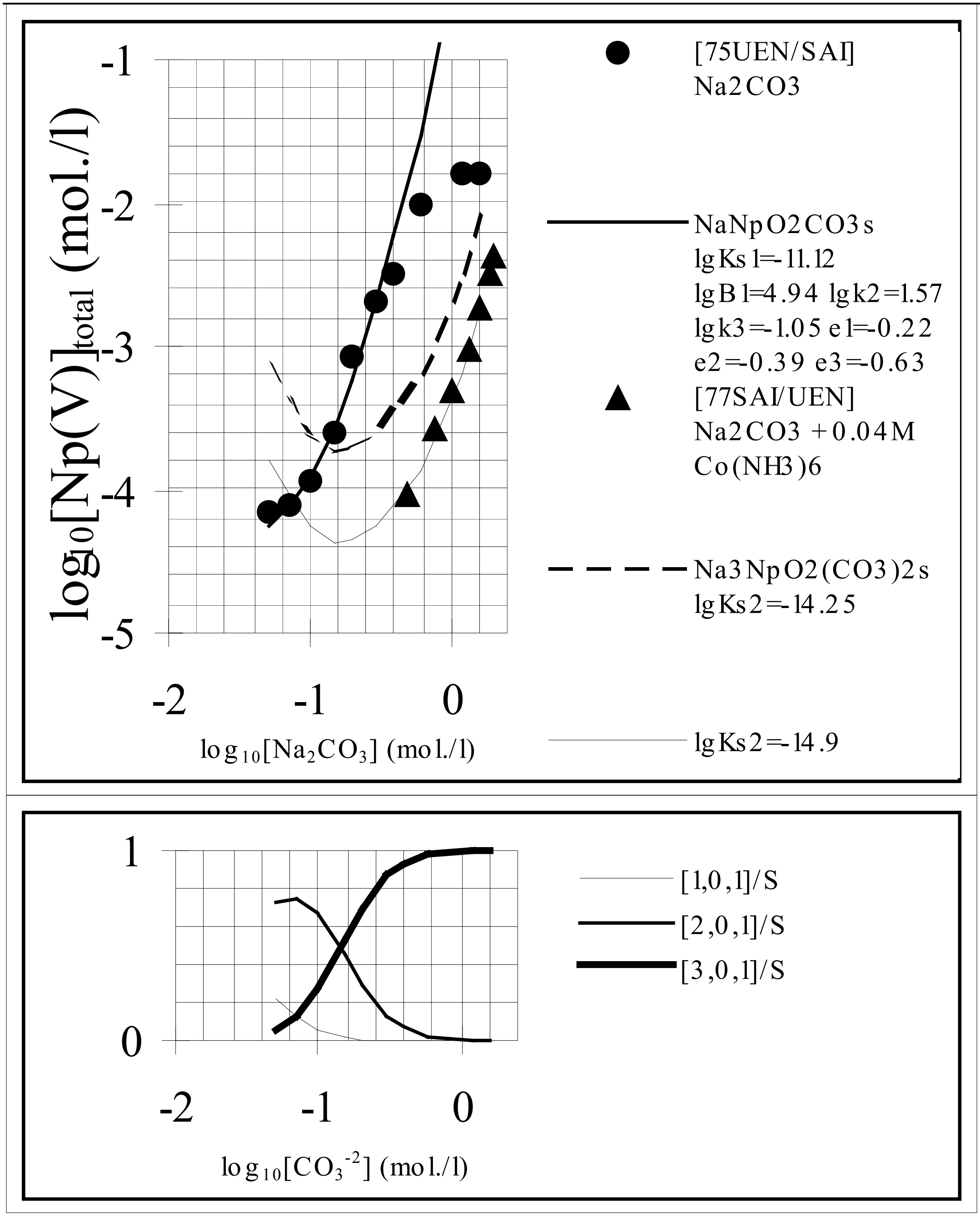


Figure [75SAI/UEN, 77SAI/UEN] Np(V) solubility in Na_2CO_3 aqueous solutions. In the upper figure, the solubility ($[Np(V)]_{total}$]) curves are calculated with the equilibrium constants and specific interaction coefficients selected by this review, except K_{s1}, the $NaNpO_2CO_{3(s)}$ solubility product, that is fitted. Its value is still in accord with the data selected by this review. The authors did not propose any interpretation or proposed other interpretations of their experimental data (see the appendix A). This figure is drawn: (a) to show that the solubility measurements reported in the [75SAI/UEN] can be interpreted as controlled by a hydrated $NaNpO_2CO_{3(s)}$ compound. At high Na_2CO_3 concentration, it is transformed into a more stable one, certainly hydrated $Na_3NpO_2(CO_3)_{2(s)}$. (b) to show that the solubility measurements reported in the [77SAI/UEN] can be interpreted as controlled by a hydrated $Na_3NpO_2(CO_3)_{2(s)}$ compound, while the authors proposed the formation of the $(Co(NH_3)_6)_8(NpO_2)_6(CO_3)_{21(s)}$ compound, whose interpretation is then rejected by the present review. ki = $[NpO_2(CO_3)_i^{1-2i}]$ / ($[NpO_2(CO_3)_{i-1}^{3-2i}]$ $[CO_3^{-2}]$), ki = k_i, B1 = β_1 = k_1, ei = $\varepsilon(NpO_2(CO_3)_i^{1-2i},Na^+)$. In the figure below [i,0,1] = $[NpO_2(CO_3)_i^{1-2i}]$, and S is Np(V) solubility. Each curve is the proportion of a soluble Np(V) species in the condition of the above figure, calculated with the same complexing constants.

[77SIM]

Experimental data scanned by this review from the figure of the [77SIM] publication, and calculations.

$\log_{10}[CO_3^{-2}]$	-0.615	-0.51	-0.42	-0.29	-0.215	-0.145	-0.13	-0.065	-0.04	-0.015
$\log_{10}[Np(V)]$	-3.51	-3.38	-3.255	-3.23	-3.175	-2.995	-3.035	-2.9	-2.965	-2.925
$\log_{10}K_{s2,3}$	-2.895	-2.87	-2.835	-2.94	-2.96	-2.85	-2.905	-2.835	-2.925	-2.91

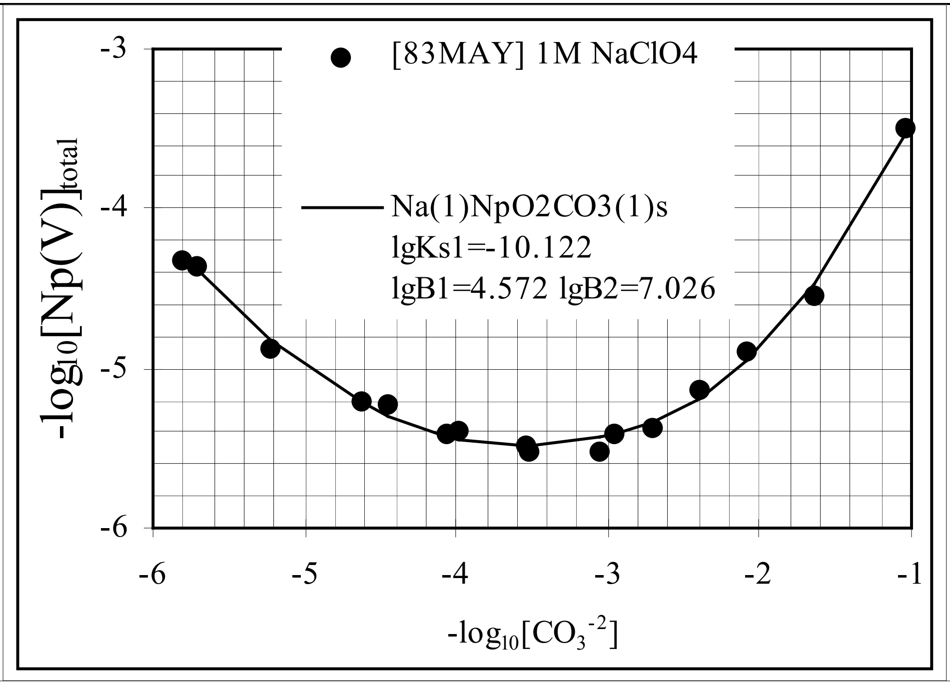
Linear regression $\log_{10}[Np(V)] = 3 \log_{10}3 - 1.469 \pm 0.045 + (0.968 \pm 0.144) \log_{10}[CO_3^{-2}]$

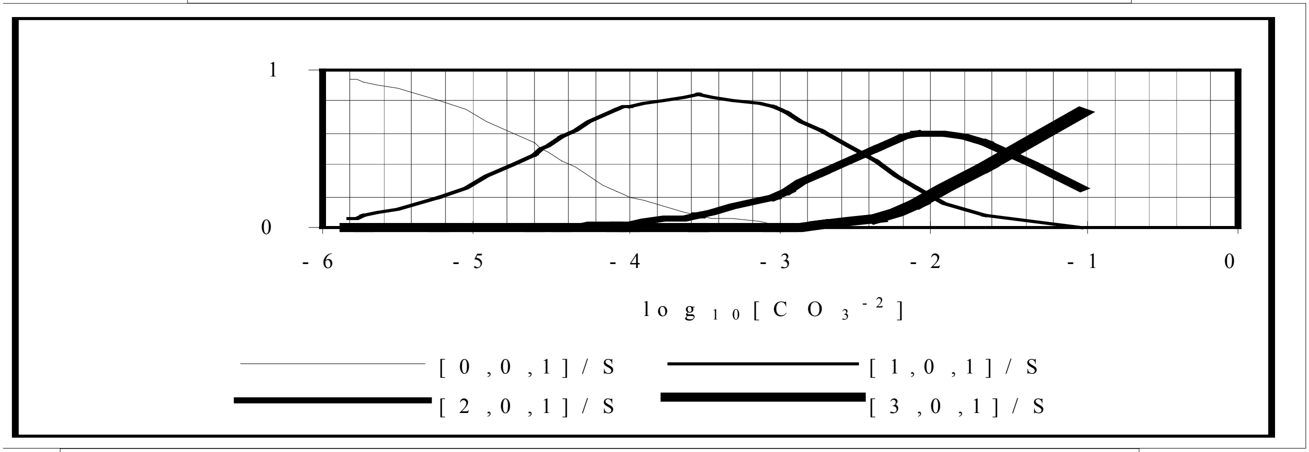
Mean $\log_{10}K_{s2,3} = 1.461 \pm 0.086$

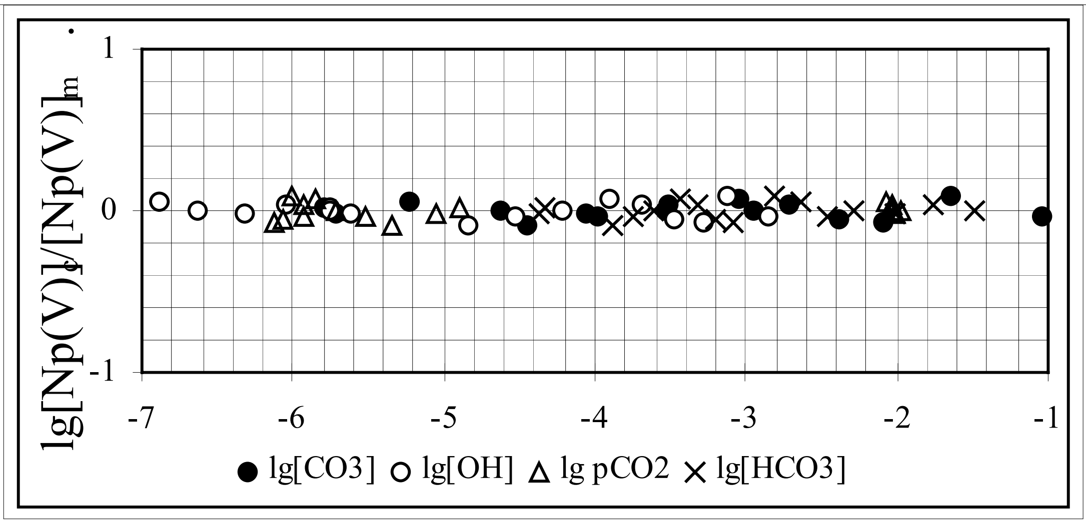
Fitted values $\log_{10}K_{s2,3} = 1.464 \pm 0.085$, for $\log_{10}k_3 = 2.51$ (over all uncertainty on $\log_{10}[Np(V)]$, 0.081),

best fit $\log_{10}K_{s2,3} = 1.475 \pm 0.085$, for $\log_{10}k_3 = \mathit{1.791}$ (over all uncertainty on $\log_{10}[Np(V)]$, 0.080)

[83MAY]







Figures [83MAY] Np(V) solubility in bicarbonate / carbonate aqueous solutions at I = 1 M ($NaClO_4$). The solubility curve (above figure) is plotted with the values fitted by this review, which are nearly the same as the ones initially proposed by Maya. They were used by this review. Ks1 = $K_{s1} = [Na^+] [NpO_2^+] [CO_3^{-2}]$ is $NaNpO_2CO_{3(s)}$ solubility product. Bi = $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / ([NpO_2^+] [CO_3^{-2}]^i)$. In the figure below, $[i,0,1] = [NpO_2(CO_3)_i^{1-2i}]$, and S is Np(V) solubility. Each curve is the proportion of a soluble Np(V) species in the condition of the above figure, calculated with the same complexing constants. Note that only the solubility measurement at $-1 = \log_{10}[CO_3^{-2}]$ is in chemical condition to have practical effect on the β_3 fitted value. The second figure is the speciation calculated with the same equilibrium constants. The lowest figure, is the residual plotted to show that there is no systematic deviation.

Experimental results from the table of the [83MAY] publication, and calculated speciation. $\log_{10}[X]$ and $-\log_{10}[H^+]$ are tabulated

	Np	H^+	CO_3^{-2}	HCO_3^-	P_{CO2}		Np	H^+	CO_3^{-2}	HCO_3^-	P_{CO2}		Np	H^+	CO_3^{-2}	HCO_3^-	P_{CO2}
1	-4.32	8.08	-5.8	-4.33	-4.89	6	-5.52	9.94	-3.05	-3.44	-5.86	6'	-4.87	6.96	-5.22	-2.63	-2.07
2	-4.36	8.21	-5.71	-4.37	-5.06	7	-5.38	10.15	-2.71	-3.31	-5.94	7'	-5.21	7.21	-4.63	-2.29	-1.98
3	-5.22	8.99	-4.44	-3.88	-5.35	8	-5.13	10.37	-2.39	-3.21	-6.06	8'	-5.41	7.51	-4.06	-2.02	-2.01
4	-5.4	9.31	-3.98	-3.74	-5.53	9	-4.89	10.55	-2.09	-3.09	-6.12	9'	-5.52	7.79	-3.52	-1.76	-2.03
5	-5.48	9.62	-3.54	-3.61	-5.71	10	-4.55	10.72	-1.64	-2.81	-6.01	10'	-5.42	8.08	-2.95	-1.48	-2.04
						11	-3.5	10.99	-1.03	-2.47	-5.94						

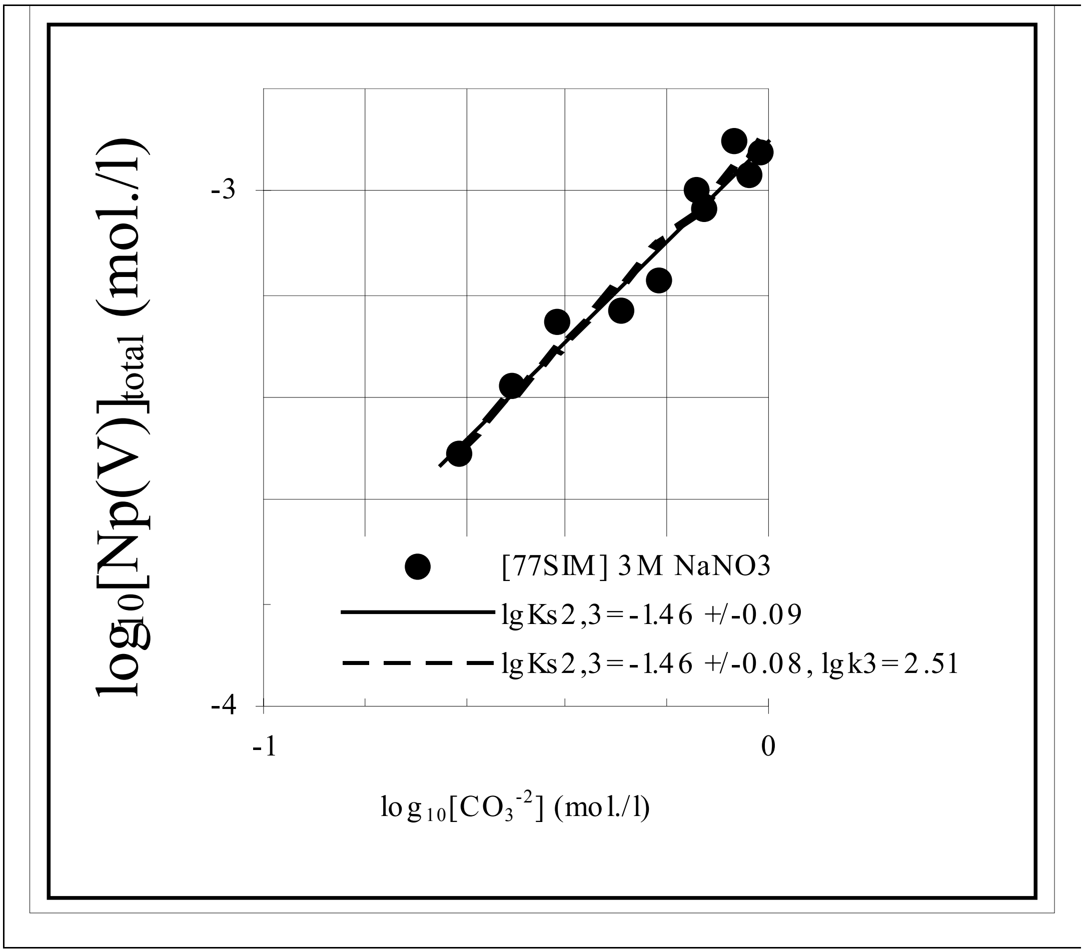


Figure [77SIM] Np(V) solubility in concentrated carbonate aqueous solution of I = 3 M ($NaNO_3$). This review followed Simakin that interpreted his solubility measurements ($[Np(V)]_{total}$]) with the $Na_3NpO_2(CO_3)_{2(s)} + CO_3^{-2} \Leftrightarrow 3\ Na^+ + NpO_2(CO_3)_3^{-5}$ equilibrium. This review calculated the corresponding equilibrium constants: $K_{s2,3}$ = Ks2,3 = $[Na^+]^3\ [NpO_2(CO_3)_3^{-5}]\ /\ [CO_3^{-2}]$, and used it to select the $Na_3NpO_2(CO_3)_{2(s)}$ solubility product. k3 = k_3 = $[NpO_2(CO_3)_3^{-5}]\ /\ ([NpO_2(CO_3)_2^{-3}]\ [CO_3^{-2}])$. Fitting k_3 does not change the results.

[85BID/TAN]

Experimental data scanned by this review from the figure of the [85BID/TAN] publication.

$lg[CO_3^{-2}]$	lgD/D°	$lg[CO_3^{-2}]$	lgD/D°	$lg[CO_3^{-2}]$	lgD/D°	$lg[CO_3^{-2}]$	lgD/D°	$lg[CO_3^{-2}]$	lgD/D°	$lg[CO_3^{-2}]$	lgD/D°
-4.18	-0.25	-3.57	-0.56	-3.47	-0.68	-3.76	-0.5	-3.27	-0.92	-2.420	-2.505
-4.12	-0.26	-3.55	-0.6	-3.45	-0.73	-3.74	-0.51	-3.21	-0.97	-2.409	-2.496
-4.1	-0.29	-3.51	-0.62	-3.4	-0.78	-3.72	-0.51	-3.17	-1	-2.377	-2.559
-4.08	-0.3	-3.47	-0.65	-3.37	-0.8	-3.69	-0.54	-3.13	-1.04	-2.347	-2.632
-3.99	-0.34	-3.4	-0.67	-3.31	-0.85	-3.56	-0.65	-3.09	-1.11	-2.337	-2.668
-3.94	-0.37	-3.37	-0.73	-3.3	-0.86	-3.54	-0.68	-3.04	-1.13	-2.319	-2.673
-3.9	-0.39	-3.87	-0.41	-3.26	-0.88	-3.53	-0.71	-3	-1.15	-2.215	-2.865
-3.83	-0.43	-3.84	-0.43	-3.25	-0.9	-3.47	-0.73	-2.95	-1.19	-2.155	-3.071
-3.8	-0.45	-3.79	-0.52	-3.18	-0.95	-3.44	-0.79	-2.523	-2.299	-2.131	-3.141
-3.76	-0.48	-3.62	-0.57	-3.16	-0.96	-3.38	-0.82	-2.481	-2.365	-2.086	-3.157
-3.72	-0.52	-3.59	-0.61	-3.12	-0.99	-3.34	-0.86	-2.444	-2.461	-2.066	-3.236
-3.67	-0.53	-3.54	-0.66	-3.8	-0.46	-3.3	-0.87	-2.432	-2.504		

Curve fitting results by this review from the experimental data of the publication [85BID/TAN]. $\log_{10}{}^*\beta_i = [NpO_2(OH)_i^{1-i}]\,[H^+]^i / [NpO_2^+]$, $\log_{10}\beta_i = [NpO_2(CO_3)_i^{1-2i}]\,[CO_3^{-2}]^{-i} / [NpO_2^+]$, Σ is the standard deviation, ± is 1.96 standard deviation.

i,j,k	$\log_{10}\beta_0$	$\log_{10}{}^*\beta_1$	$\log_{10}{}^*\beta_2$	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	Σ	±	$\log_{10}k_2$	$\log_{10}k_3$
		-11	-23	4.13	7.06	9	0.137688	0.270		
weighted mean	-0.037			4.137	7.070	8.878			2.938	1.921
±	0.034			0.011	0.042	2.123			0.019	0.057
a priori		-11	-23	4.210	6.460	7.250	0.270685	0.531		
weighted mean	-0.044			4.217	6.478	7.245			2.267	0.815
±	0.025			0.014	0.115	1.043			0.056	0.180
		-11	-23	4.019	6.450	9.508	0.056137	0.110		
weighted mean	0.005			4.018	6.439	9.315			2.420	2.996
±	0.024			0.008	0.114	2.637			0.056	0.062
		-91.594	-27.245	4.020	6.449	9.508	0.056102	0.110		
weighted mean		-91.594	-27.245	4.018	6.438	9.315	0.093224	0.183	2.419	2.998
±				0.008	0.114	2.637	0.093229	0.183	0.057	0.062
		-11	-23	3.800	7.223	7.25	0.092875	0.182		
weighted mean	-0.023			3.785	7.217	7.172			3.418	0.093
±	0.039			0.055	0.057	2.068			0.021	0.255

[85INO/TOC]

Experimental data scanned by this review.

lg$[CO_3^{-2}]$	lgD/D°	lg$[CO_3^{-2}]$	lgD/D°	lg$[CO_3^{-2}]$	lgD/D°	lg$[CO_3^{-2}]$	lgD/D°	lg$[CO_3^{-2}]$	lgD/D°	lg$[CO_3^{-2}]$	lgD/D°
-7.48	0	-5.59	0	-4.71	-0.06	-4.12	-0.31	-3.47	-0.8	-2.41	-2.2
-7.18	0	-5.59	-0.02	-4.7	-0.12	-4.06	-0.4	-3.42	-0.87	-5.42	-0.02
-6.92	0	-5.44	0	-4.62	-0.13	-4.05	-0.36	-3.36	-0.9	-5.1	-0.04
-6.6	0	-5.37	0	-4.6	-0.15	-4.02	-0.34	-3.28	-0.92	-4.82	-0.08
-6.44	0	-5.3	0	-4.58	-0.12	-3.97	-0.44	-3.27	-0.98	-4.51	-0.15
-6.32	-0.01	-5.3	-0.02	-4.53	-0.1	-3.95	-0.4	-3.2	-1.05	-4.32	-0.19
-6.37	-0.01	-5.28	0	-4.5	-0.14	-3.9	-0.47	-3.16	-1.1	-4.16	-0.28
-6.14	0	-5.25	-0.01	-4.5	-0.16	-3.87	-0.4	-3	-1.33	-4.04	-0.35
-6.02	-0.01	-5.18	-0.01	-4.45	-0.13	-3.86	-0.5	-2.99	-1.28	-3.9	-0.42
-6.07	0	-5.11	-0.01	-4.44	-0.17	-3.82	-0.52	-2.97	-1.35	-3.75	-0.55
-5.95	0	-5.03	-0.02	-4.38	-0.19	-3.82	-0.55	-2.85	-1.56	-3.58	-0.66
-5.9	-0.01	-4.98	-0.03	-4.35	-0.16	-3.7	-0.54	-2.82	-1.57	-3.49	-0.77
-5.85	0	-4.96	-0.04	-4.33	-0.22	-3.68	-0.63	-2.78	-1.63	-3.28	-0.97
-5.73	0	-4.91	-0.03	-4.28	-0.21	-3.67	-0.58	-2.68	-1.78	-2.9	-1.61
-5.77	0	-4.81	-0.08	-4.2	-0.2	-3.62	-0.63	-2.59	-1.85	-2.8	-1.79
-5.65	-0.01	-4.81	-0.12	-4.17	-0.31	-3.6	-0.7	-2.58	-1.9		
-5.64	0	-4.75	-0.1	-4.13	-0.23	-3.59	-0.68	-2.46	-2.07		

Curve fitting results by this review from the experimental data of the publication [85INO/TOC]. $\log_{10}{}^*\beta_i = [NpO_2(OH)_i^{1-i}]\,[H^+]^i / [NpO_2^+]$, $\log_{10}\beta_i = [NpO_2(CO_3)_i^{1-2i}]\,[CO_3^{-2}]^{-i} / [NpO_2^+]$, Σ is the standard deviation, ± is 1.96 standard deviation. $k_i = k_i / k_{i-1}$.

i,j,k	$\log_{10}\beta_0$	$\log_{10}{}^*\beta_1$	$\log_{10}{}^*\beta_2$	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	Σ	±	$\log_{10}k_1$	$\log_{10}k_2$	$\log_{10}k_3$
				4.14	6.78	8.44	0.039317	0.077			
weighted mean	0.0087			4.146	6.781	8.444			4.142	2.640	1.666
±	0.0279			0.054	0.005	0.082			0.020	0.002	0.039
expected		-11	-23	4.15	6.75	8.44	0.040441	0.079			
weighted mean	0.0097			4.158	6.751	8.445			4.152	2.601	1.697
±	0.0280			0.054	0.006	0.086			0.020	0.003	0.040
fit				4.112	6.840	8.440	0.038082	0.075			
weighted mean	0.0059	-11	-23	4.115	6.840	8.441			4.113	2.728	1.605
±	0.0280			0.056	0.003	0.080			0.021	0.001	0.032
fit		-11	-23	4.106	6.880	0.843	0.037253	0.073			
weighted mean	0.0055			4.108	6.880	4.768			4.108	2.774	-2.112
±	0.0281			0.057	0.003	2.003			0.022	0.001	0.871

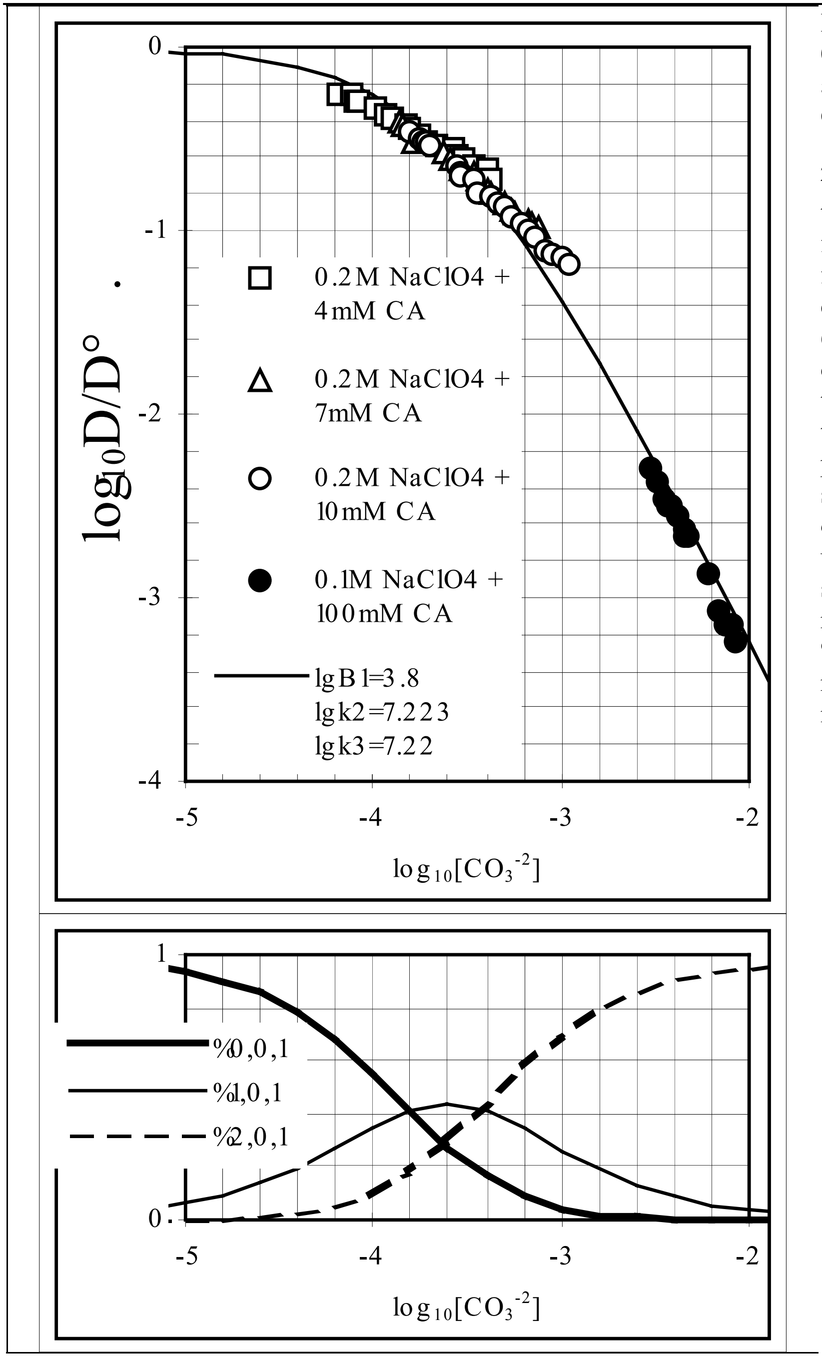
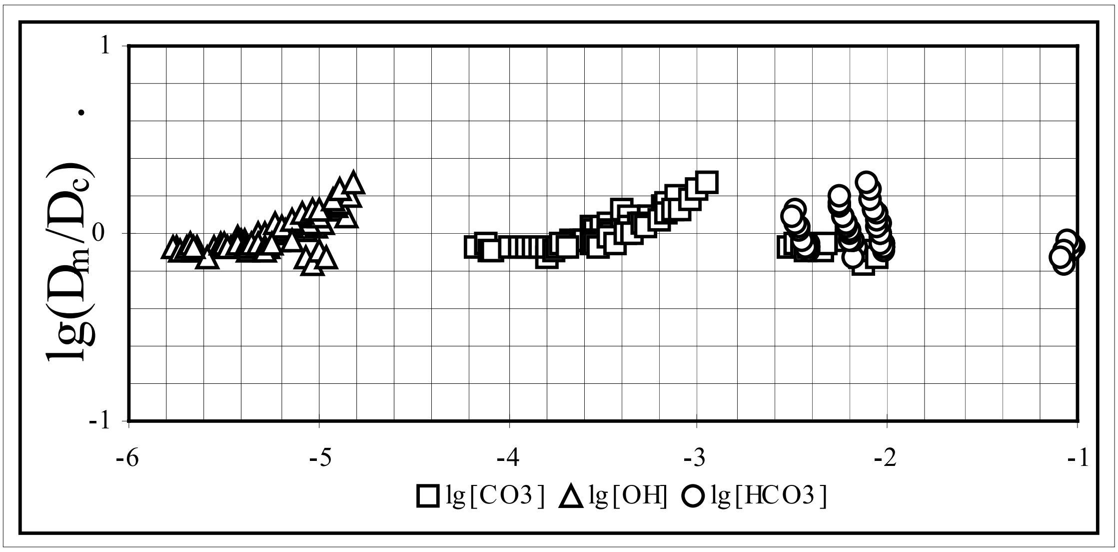


Figure [85BID/TAN] Np(V) extraction from 0.1 or 0.2 M $NaClO_4$ bicarbonate / carbonate aqueous solutions. D is the partition coefficient. CA is the total carbonate concentration. ki = k_i = $[NpO_2(CO_3)_i^{1-2i}]$ / $([NpO_2(CO_3)_{i-1}^{3-2i}]$ $[CO_3^{-2}])$, B1 = β_1 = k_1. The curve is calculated with the values fitted by this review (written on the figure); except the k_3 value that could not be fitted (as pointed out by the authors), its value is calculated from the data selected by this review (from other experimental studies). The authors did not use the same graphical presentation of their experimental results, and did not plot all of them on the same figure. This figure is plotted to point out that it was not possible to avoid systematic deviation between the different series of experimental data. This could be due to some uncontrolled experimental change between these series, or to unrecognised side reaction. For this reason, this review did not consider these data. %i,0,1 is the $[NpO_2(CO_3)_i^{1-2i}]$ / $[Np(V)]_{total}$ ratio. D_c is the calculated D value, D_m is the measured one.



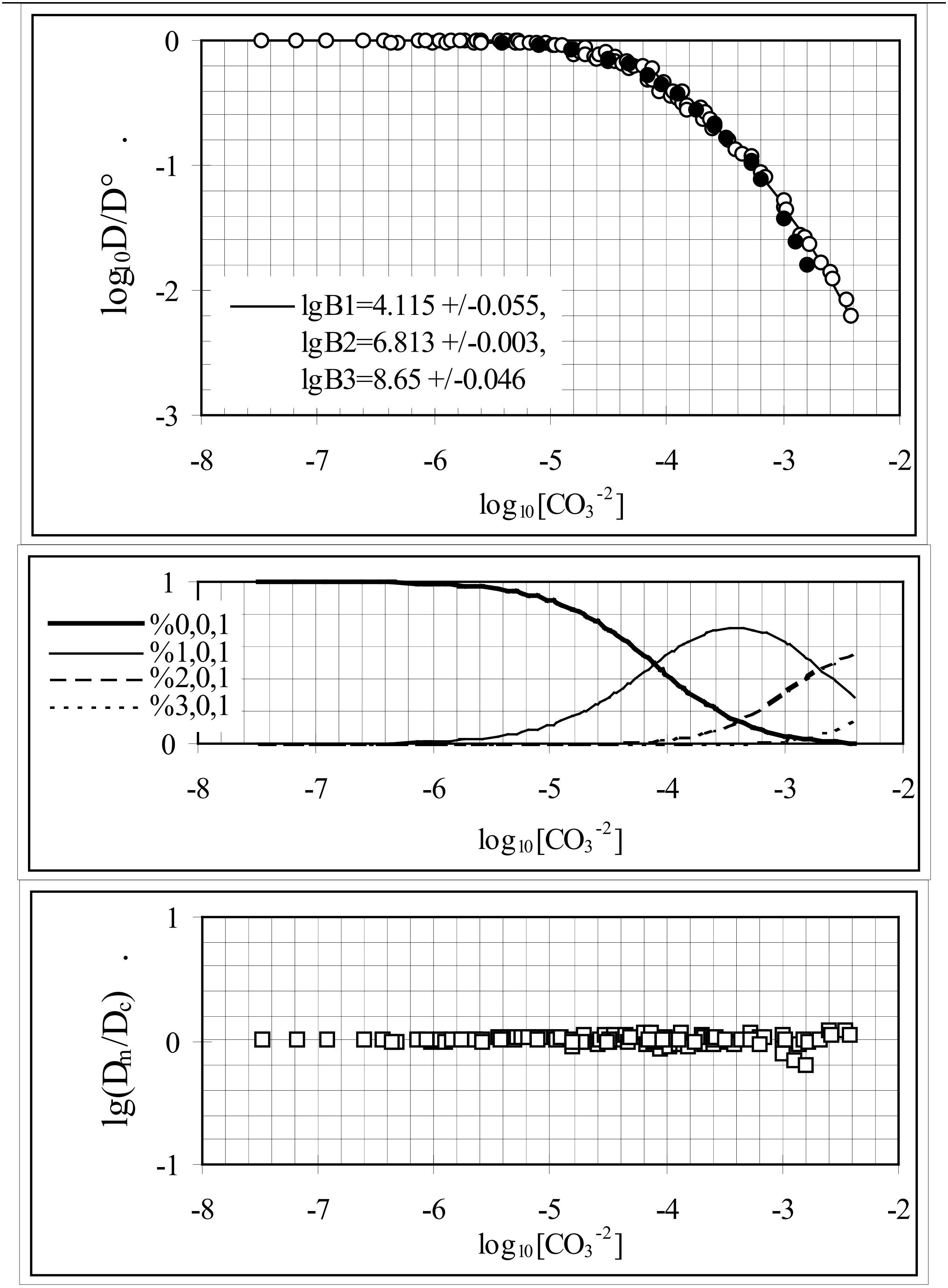


Figure [85INO/TOC] Np(V) extraction from 1 M $NaClO_4$ bicarbonate / carbonate aqueous solutions. D is the partition coefficient. Bi = β_i = $[NpO_2(CO_3)_i^{1-2i}]$ / ($[NpO_2^+]$ $[CO_3^{-2}]^i$). The curve is calculated with the values fitted by this review (written on the figure); except the β_3 value that could not be fitted (as pointed out by the authors), its value is calculated from the data selected by this review (from other experimental studies). %i,0,1 is the $[NpO_2(CO_3)_i^{1-2i}]$ / $[Np(V)]_{total}$ ratio. This review did not consider these data (see the Appendix A). Systematic deviation is here less important than for the [85BID/TAN] data (see the corresponding figures). D_c is the calculated D value, D_m is the measured one.

[90NIT/STA]

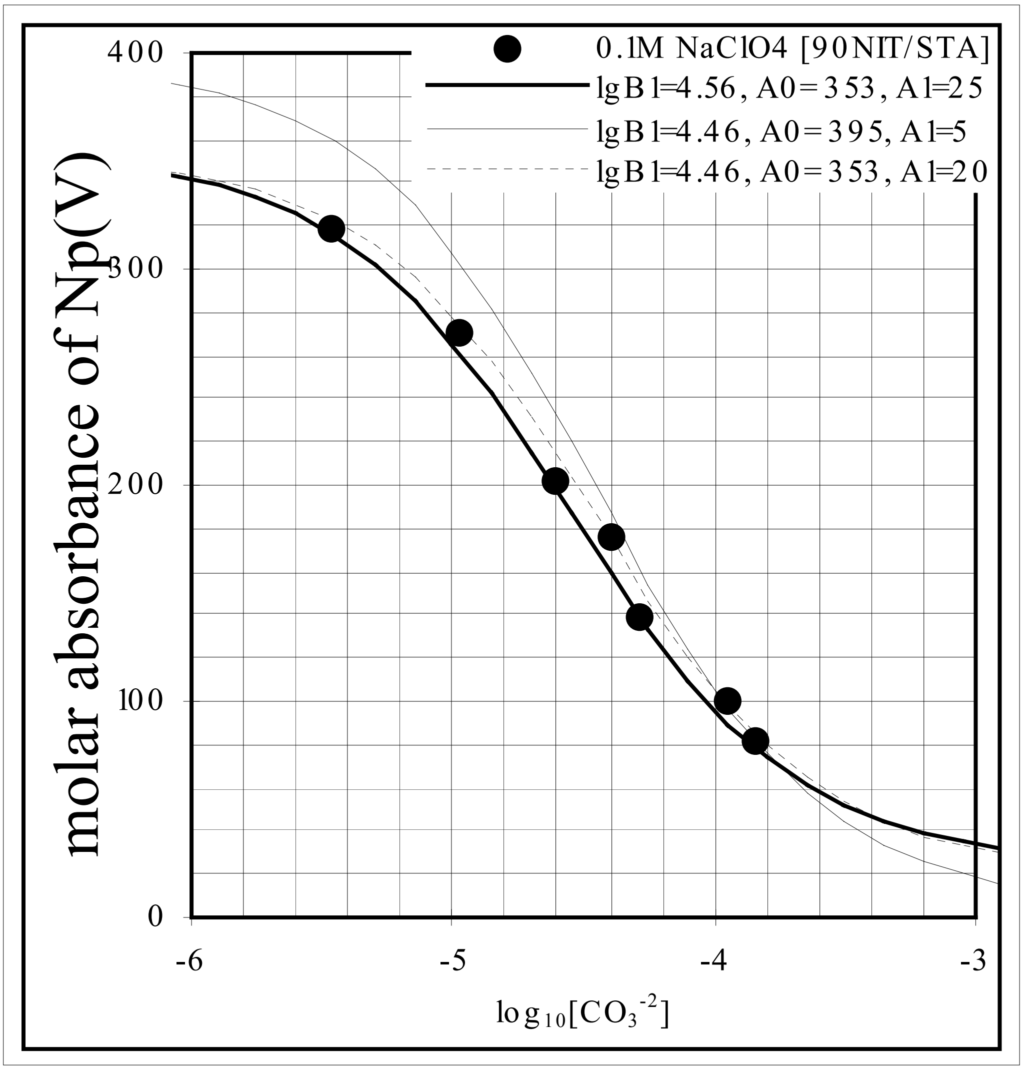
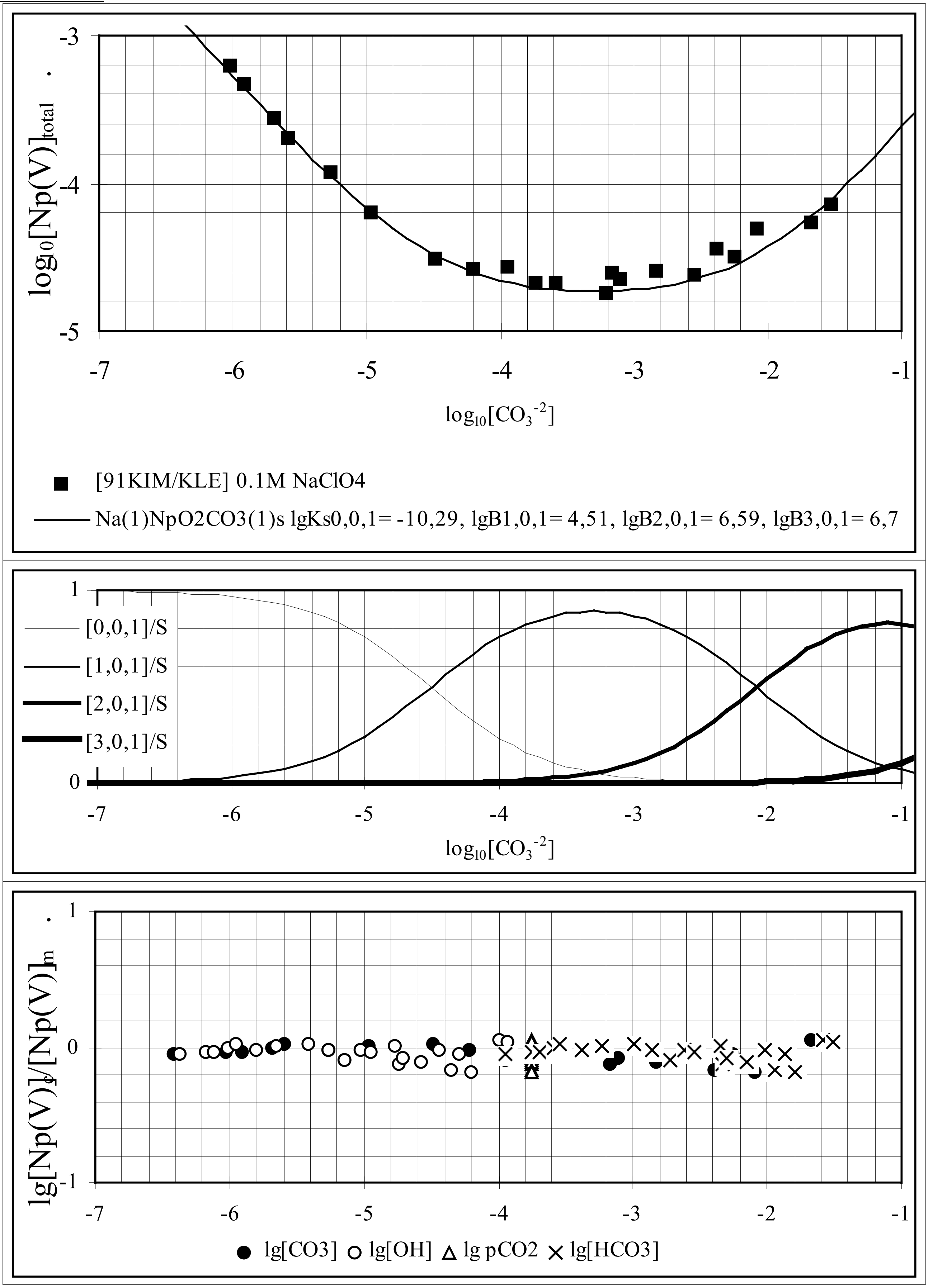


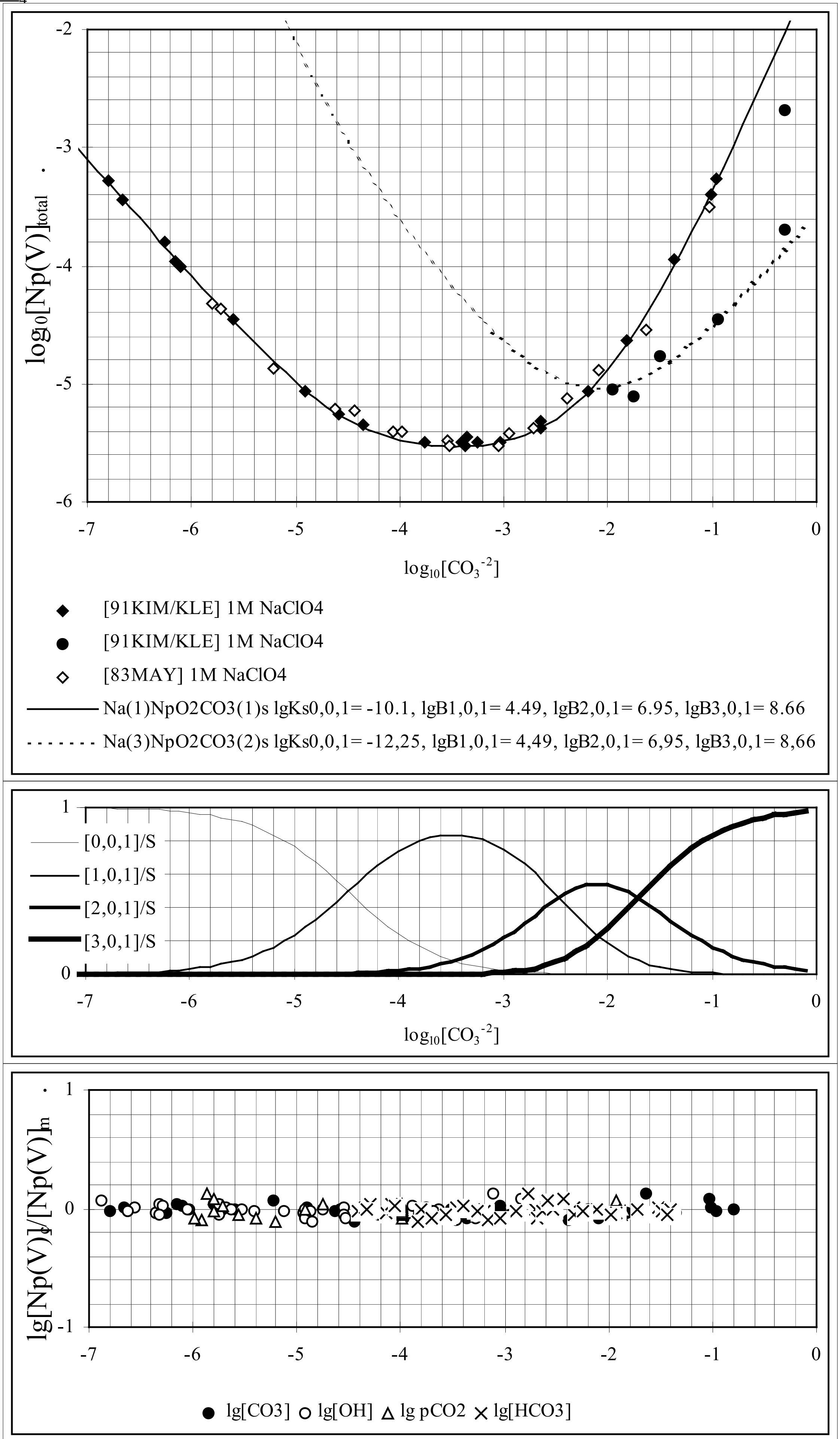
Figure [90NIT/STA]: Spectrophotometric determination of $NpO_2CO_3^-$ formation constant, β_1 = B1 = $[NpO_2CO_3^-]$ / $([NpO_2^+]\ [CO_3^{-2}])$. The points are the experimental measurements. A0 and A1 are the NpO_2^+ and $NpO_2CO_3^-$ molar absorptivity coefficients. The present review tested several interpretations (following the authors'one) for the reasons explained in the Appendix A. This review proposes the one corresponding to the bolded curve, where A0, A1 and β_1 were fitted, where hydrolysis was neglected, which is consistent with the data for Np(V) hydrolysis constants proposed by this review; but not with the original interpretation of the authors. Note that A0 fitted value is consistent with the well established one (400±10 $l.mol.^{-1}.cm^{-1}$)

[91KIM/KLE, 94NEC/KIM] comparisons with other published solubility measurements

0.1 M NaClO4

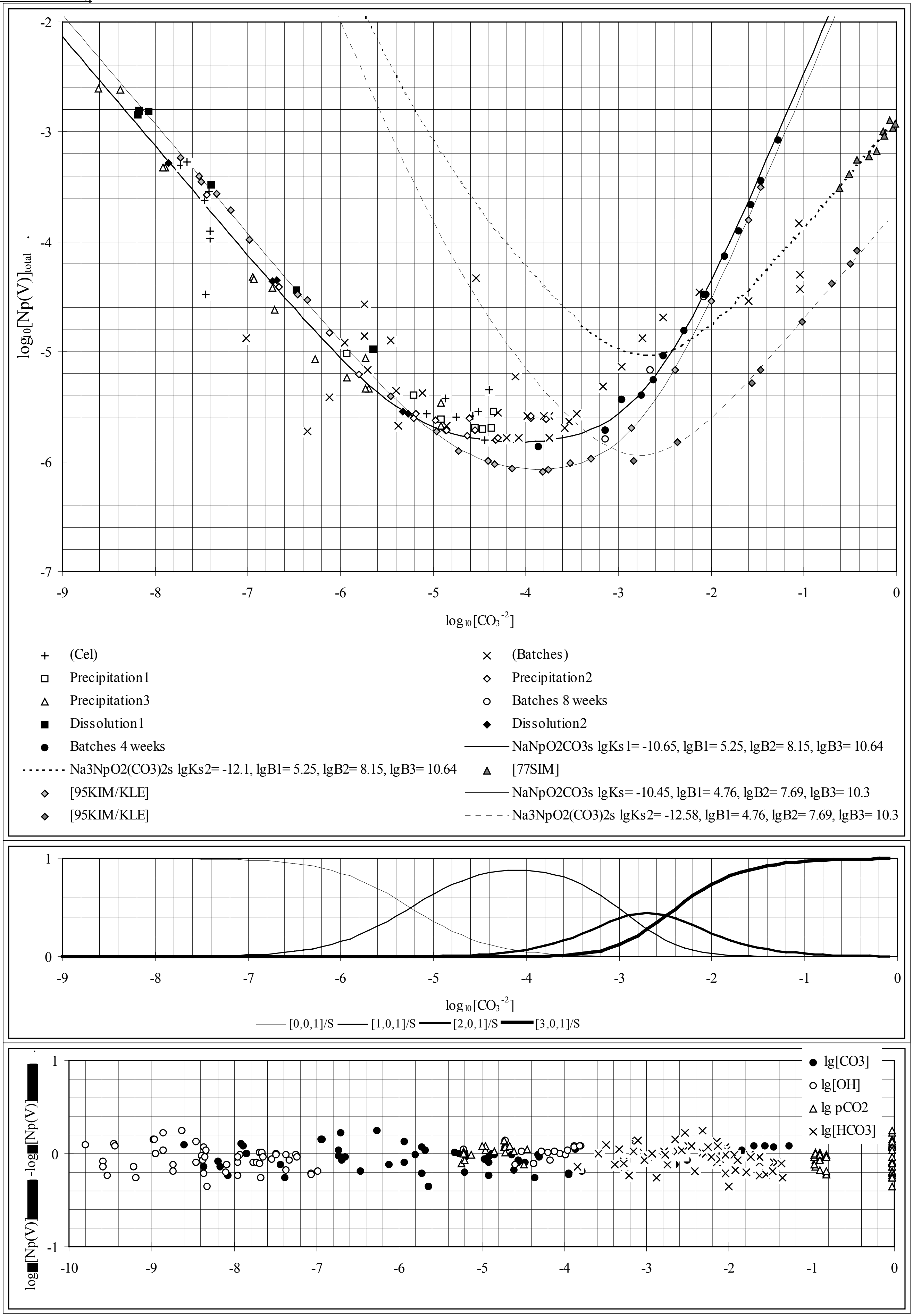


1 M $NaClO_4$



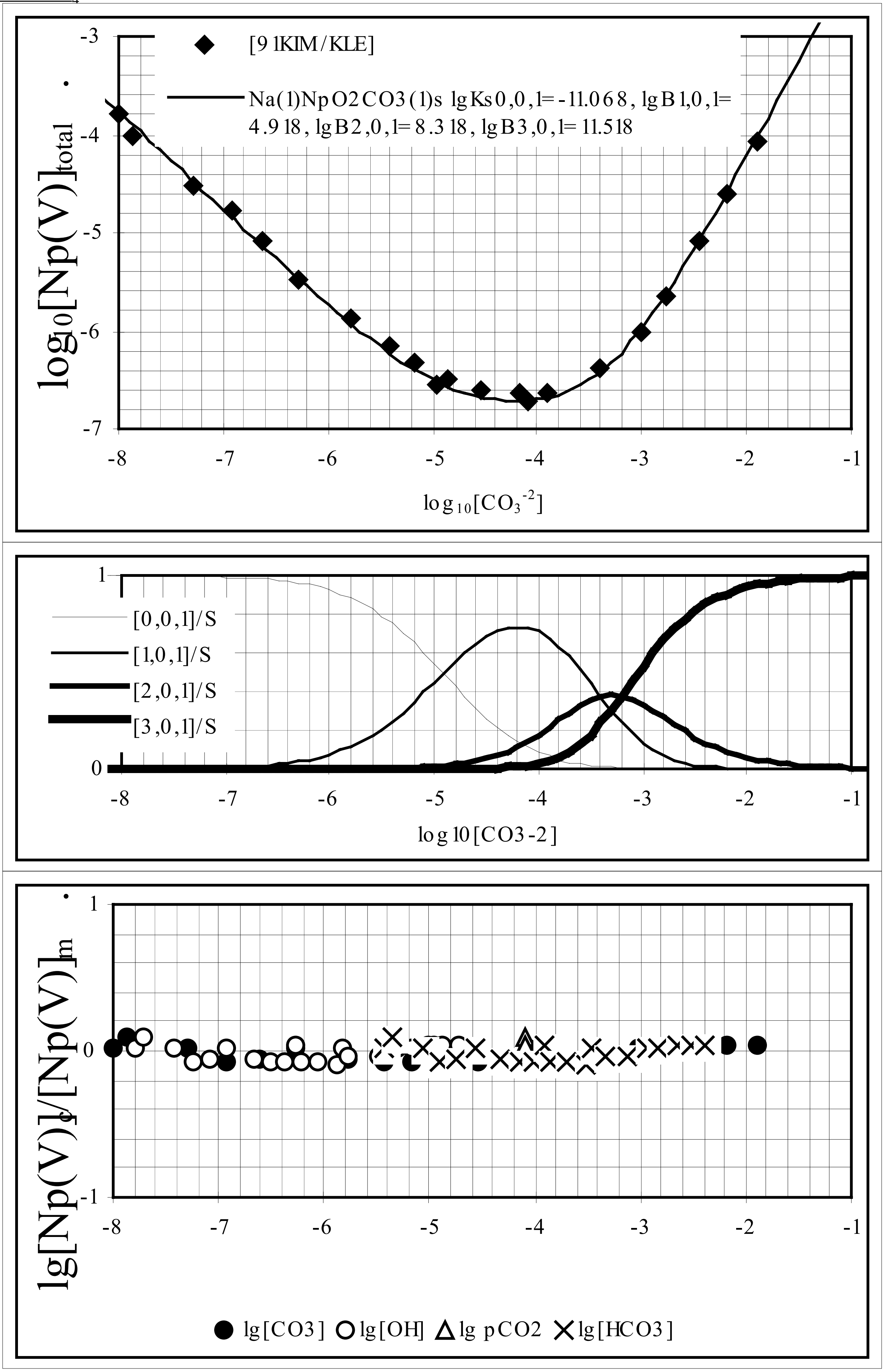
Bi,0,1 = Bi = $\beta_i = [NpO_2(CO_3)_i^{1-2i}] / [NpO_2^+] [CO_3^{2-}]^i$, Ks0,0,1 = $K_s = [M^+]^{2i-1} [NpO_2^+] [CO_3^{2-}]^i$ is the solubility product of the compound written o,n the figure. S = $[Np(V)]_{total}$ is the solubility. [i,0,1] = $[NpO_2(CO_3)_i^{1-2i}]$. $[Np(V)]_c = [Np(V)]_{calculated}$, $[Np(V)]_m = [Np(V)]_{measured}$.

3 M $NaClO_4$



Bi = β_i = $[NpO_2(CO_3)_i^{1-2i}]$ / $[NpO_2^+]$ $[CO_3^{2-}]^i$, ki = $k_i = \beta_i / \beta_{i-1}$, Ks0,0,1 = K_{si} = $[M^+]^{2i-1}$ $[NpO_2^+]$ $[CO_3^{2-}]^i$ is the solubility product of the compound written o,n the figure. S = $[Np(V)]_{total}$ is the solubility. [i,0,1] = $[NpO_2(CO_3)_i^{1-2i}]$. When nothing else is stated, the experimental data are from [86GRE/ROB]. $[Np(V)]_c$ = $[Np(V)]_{calculated}$, $[Np(V)]_m$ = $[Np(V)]_{measured}$.

5 M $NaClO_4$


[91KIM/KLE]
Na(1)NpO2CO3(1)s lgKs0,0,1=-11.068, lgB1,0,1= 4.918, lgB2,0,1=8.318, lgB3,0,1=11.518
log10[Np(V)]total
log10[CO3-2]
-3
-4
-5
-6
-7
-8
-7
-6
-5
-4
-3
-2
-1
[0,0,1]/S
[1,0,1]/S
[2,0,1]/S
[3,0,1]/S
1
0
log10[CO3-2]
lg[Np(V)]c/[Np(V)]m
1
0
-1
● lg[CO3] ○ lg[OH] △ lg pCO2 ✕ lg[HCO3]

[93LEM/BOY]

The references (ref.) are 1: [83MAY] reinterpreted in [93LEM/GOR], 2: [93LEM/GOR], 3: calculated from [93LEM/GOR] equilibrium constants, 4: [83MAY] reinterpreted by this review, 5: [93LEM/GOR] reinterpreted by this review, 6: as 5 K^+. K_{si} is $Na_{2i-1}NpO_2(CO_3)_{i(s)}$ solubility product. $K_{ss} = K_{s2} / K_{s1}$ $K_{si}\beta_j$ is also noted $K_{si,j}$. Some of the equilibrium constants are calculated from the other ones (on the same line).

ref.	$[Na^+]$	°C	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	$\log_{10}k_2$	$\log_{10}k_3$	$\log_{10}K_{s1}$	$\log_{10}K_{s1}\beta_1$
1	1	25	4.6 ± 0.1	7.1 ± 0.1	8.5 ± 0.1	2.5 ± 0.14	1.4 ± 0.14	-10.12 ± 0.04	-5.52 ± 0.11
2^a	1	30	4.7 ± 0.1	7 ± 0.1		2.3 ± 0.14		-10.7 ± 0.1	-6 ± 0.14
2^a	1	50	5.6 ± 0.2	6.9 ± 0.3	8.6 ± 0.3	1.3 ± 0.36	1.7 ± 0.42	-11 ± 0.1	-5.4 ± 0.22
3^a	1	75	5.80 ± 0.58	8.80 ± 1.62	10.10 ± 1.42	3 ± 1.52	1.3 ± 1.41	-10.94 ± 0.29	-5.14 ± 0.51
4	1	25	4.57 ± 0.35	7.03 ± 0.24	8.52 ± 0.41	2.45 ± 0.26	1.5 ± 0.36	-10.12 ± 0.35	-5.55 ± 0.35
5^a	1	30	4.77 ± 0.51	7.47 ± 0.54	8.97 ± 0.58	2.7 ± 0.22	1.5 ± 0.22	-10.77 ± 0.5	-6 ± 0.1
5^a	1	50	5.7 ± 0.54	8.80 ± 0.57	10.30 ± 0.66	3.1 ± 0.18	1.5 ± 0.34	-11.1 ± 0.2	-5.4 ± 0.5
5	1	75	5.2 ± 0.54	7.30 ± 0.61	8.90 ± 0.61	2.1 ± 0.28	1.6 ± 0.28	-10.5 ± 0.5	-5.3 ± 0.2
5^a	0.5	75	4.8 ± 0.28	7.20 ± 0.36	8.55 ± 0.56	2.40 ± 0.36	1.35 ± 0.42	-9.80 ± 0.2	-5.00 ± 0.2
6	1	75				2.2 ± 0.4	2.5 ± 0.45		-6.7 ± 0.2
2	1	75	5.6 ± 0.3		9.3 ± 0.7			-10.8 ± 0.2	-5.2 ± 0.36
2	1	75	6.3 ± 0.7	9.3 ± 0.9		3 ± 1.14		-11.3 ± 0.5	-5 ± 0.86

ref.	$[Na^+]$	°C	$\log_{10}K_{s1}\beta_2$	$\log_{10}K_{s1}\beta_3$	$\log_{10}K_{s2}$	$\log_{10}K_{s2}\beta_1$	$\log_{10}K_{s2}\beta_2$	$\log_{10}K_{s2}\beta_3$	$\log_{10}K_{ss}$
1	1	25	-3.02 ± 0.11	-1.62 ±					
2^a	1	30	-3.70 ± 0.14						
2^a	1	50	-4.10 ± 0.32	-2.4 ± 0.32	-12.90 ± 0.22	-7.3 ± 0.3	-6 ± 0.37	-4.3 ± 0.37	-1.9 ± 0.2
3^a	1	75	-2.14 ± 1.60	-0.84 ± 1.39	-14.40 ± 1.15	-8.6 ± 0.99	-5.6 ± 1.14	-4.3 ± 0.83	-3.46 ± 1.12
4	1	25	-3.1 ± 0.24	-1.6 ± 0.41					
5^b	1	30	-3.3 ± 0.2		-13.47 ± 0.55	-8.7 ± 0.24	-6 ± 0.1	-4.5 ± 0.2	-2.7 ± 0.22
5^a	1	30	-2.3 ± 0.53	-1.8 ± 0.3	-12.97 ± 0.62	-8.2 ± 0.37	-5.5 ± 0.41	-4 ± 0.2	-2.2 ± 0.36
5^a	1	50	-3.2 ± 0.35	-0.8 ± 0.59	-14.8 ± 0.55	-9.1 ± 0.1	-6 ± 0.15	-4.5 ± 0.3	-3.7 ± 0.51
5^a	1	75	-2.6 ± 0.3	-1.6 ± 0.35	-13.4 ± 0.57	-8.2 ± 0.2	-6.1 ± 0.2	-4.5 ± 0.2	-2.9 ± 0.28
5	0.5	75	-4.5 ± 0.45	-1.25 ± 0.52	-13.25 ± 0.47	-8.45 ± 0.47	-6.05 ± 0.3	-4.70 ± 0.3	-3.45 ± 0.42
6	1	75		-2 ± 0.63		-9.4 ± 0.63	-7.2 ± 0.4	-4.7 ± 0.2	-2.7 ± 0.6
2	1	75	-2 ± 1.03	-1.5 ± 0.73	-13.6 ± 0.45	-8 ± 0.54		-4.3 ± 0.83	-2.8 ± 0.4
2	1	75			-14.9 ± 0.71	-8.6 ± 0.99	-5.6 ± 1.14		-3.6 ± 0.5

[a]Values used below for Δ_rH_{mean} and Δ_rS_{mean} evaluation. [b]Low temperature $Na_3NpO_2(CO_3)_{2(s)}$ hydrated compound.

From each equilibrium constant, K, lnK = 2.30258509299405 $\log_{10}K$ was calculated, and then $\Delta_rG = -0.0083145107\ T\ \ln K$ (kJ mol.$^{-1}$), $\mathbf{\Delta_rS_{mean}} = -1000\delta(\Delta_rG)/\delta t$ (J mol.$^{-1}$ K^{-1}), $\Delta_rH_{mean1} = \Delta_rG_{mean} + \Delta_rS_{mean}\ T_{mean} / 1000$ (kJ mol.$^{-1}$), $\Delta_rH_{mean2} = -0.0083145107\ \delta(\ln K) / \delta(1/T)$ (kJ mol.$^{-1}$), where X_{mean} is the mean value of X at different temperatures (same column), δX is X maximum variations with t ($X_{max} - X_{min}$ among the same column). All the Δ_rS and Δ_rH values tabulated below are Δ_rS_{mean} and Δ_rH_{mean} values where the subscript$_{mean}$ is not written.

ref.	$[Na^+]$	°C	Δ_rS_1	Δ_rS_2	Δ_rS_3	Δ_rS_2-Δ_rS_1	Δ_rS_3-Δ_rS_1	Δ_rS_{s1}	$\Delta_rS_{s1,1}$
2	1	40	379±223	554±235	583±265	175±086	29±122	-308±158	71±157
2	1	62.5	-24±196	-231±215	-176±230	-207±088	55±112	-53±142	-77±135
3	1	52.5	155±103	118±114	161±-117	-37±051	44±051	-166±098	-11±032
5	1	40	368±068	103±097		-265±119		-298±042	71±080
5	1	62.5	161±163	639±439	565±386	478±414	-74±391	-195±080	-34±146
5	1	52.5	253±087	401±241		148±225		-241±044	12±077

ref.	$[Na^+]$	°C	$\Delta_rS_{s1,2}$	$\Delta_rS_{s1,3}$	Δ_rS_{s2}	$\Delta_rS_{s2,1}$	$\Delta_rS_{s2,2}$	$\Delta_rS_{s2,3}$	Δ_rS_{ss}
2	1	40	246±174	275±203	-814±246	-435±113	-260±128	-231±109	-506±189
2	1	62.5	-284±161	-229±173	90±205	66±059	-142±065	-86±091	142±147
3	1	52.5	-48±057	-5±064	-312±116	-157±-57	-194±061	-151±039	-146±063
5	1	40	-195±106						
5	1	62.5	444±434	370±379	-647±312	-486±275	-8±319	-82±240	-452±302
5	1	52.5	160±238						

$\Delta_r\mathbf{H}_{\mathbf{mean1}} = \Delta_r G_{mean} + \Delta_r S_{mean} T_{mean} / 1000$ (kJ mol.$^{-1}$)

ref.	[Na$^+$]	°C	Δ_rH_1	Δ_rH_2	Δ_rH_3	Δ_rH_2-Δ_rH_1	Δ_rH_3-Δ_rH_1	Δ_rH_{s1}	$\Delta_rH_{s1,1}$
2	1	40	87.2±69.8	124.7±73.7	124.7±083.0	37.5±026.8	0.0±038.3	-30.9±49.4	56.3±49.3
2	1	62.5	-43.1±65.8	-129.2±72.1	-120.6±077.3	-86.2±029.4	8.6±037.7	51.7±47.8	8.6±45.3
3	1	52.5	19.3±33.7	-7.6±37.1	-3.1±038.3	-26.9±016.6	4.5±016.6	12.1±32.1	31.4±10.5
5	1	40	84.4±21.4	-9.4±30.5		-93.8±037.2		-28.1±13.3	56.3±25.2
5	1	62.5	17.4±54.8	163.9±147.6	129.4±129.7	146.5±139.1	-34.5±131.5	4.9±26.9	22.3±49.2
5	1	52.5	49.5±28.5	80.9±78.7		31.4±073.6		-10.9±14.4	38.6±25.3

ref.	[Na$^+$]	°C	$\Delta_rH_{s1,2}$	$\Delta_rH_{s1,3}$	Δ_rH_{s2}	$\Delta_rH_{s2,1}$	$\Delta_rH_{s2,2}$	$\Delta_rH_{s2,3}$	Δ_rH_{ss}
2	1	40	93.8±54.6	93.8±063.5	-171.6±077.2	-84.4±35.4	-46.9±040.2	-46.9±34.3	-140.7±059.3
2	1	62.5	-77.5±54.0	-68.9±058.1	120.6±068.7	77.5±19.7	-8.6±021.8	0.0±30.7	68.9±049.4
3	1	52.5	4.5±18.7	9.0±021.0	-19.3±038.0	0.0±18.5	-26.9±019.9	-22.5±12.8	-31.4±020.4
5	1	40	-37.5±33.2						
5	1	62.5	168.8±145.6	134.3±127.4	-129.4±104.9	-112.0±92.5	34.5±107.1	0.0±80.6	-134.3±101.4
5	1	52.5	70.0±77.6						

$\Delta_r\mathbf{H}_{\mathbf{mean2}} = -0.0083145107\ \delta(\ln K) / \delta(1/T)$ (kJ mol.$^{-1}$)

ref.	[Na$^+$]	°C	Δ_rH_1	Δ_rH_2	Δ_rH_3	Δ_rH_2-Δ_rH_1	Δ_rH_3-Δ_rH_1	Δ_rH_{s1}	$\Delta_rH_{s1,1}$
2	1	40	87.1±70.1	125.1±73.1	125.1±083.1	38.1±027.1	0.1±038.1	-31.1±50.1	56.1±48.1
2	1	62.5	-43.1±66.1	-129.1±72.1	-121.1±077.1	-86.1±029.1	9.1±038.1	52.1±46.1	9.1±46.1
3	1	52.5	19.1±33.1	-8.1±36.1	-3.1±038.1	-27.1±016.1	4.1±016.1	12.1±32.1	31.1±10.1
5	1	40	84.1±21.1	-9.1±30.1		-94.1±036.1		-28.1±13.1	56.1±25.1
5	1	62.5	17.1±53.1	164.1±142.1	129.1±125.1	146.1±134.1	-34.1±127.1	5.1±26.1	22.1±48.1
5	1	52.5	49.1±27.1	81.1±73.1		31.1±068.1		-11.1±14.1	39.1±24.1

ref.	[Na$^+$]	°C	$\Delta_rH_{s1,2}$	$\Delta_rH_{s1,3}$	Δ_rH_{s2}	$\Delta_rH_{s2,1}$	$\Delta_rH_{s2,2}$	$\Delta_rH_{s2,3}$	Δ_rH_{ss}
2	1	40	94.1±53.1	94.1±062.1	-172.1±077.1	-84.1±36.1	-47.1±041.1	-47.1±34.1	-141.1±59.1
2	1	62.5	-78.1±55.1	-69.1±059.1	121.1±068.1	78.1±19.1	-9.1±022.1	0.1±31.1	69.1±50.1
3	1	52.5	4.1±18.1	9.1±021.1	-19.1±038.1	0.1±19.1	-27.1±021.1	-22.1±13.1	-31.1±21.1
5	1	40	-38.1±32.1						
5	1	62.5	169.1±140.1	134.1±123.1	-129.1±101.1	-112.1±90.1	34.1±104.1	0.1±78.1	-134.1±98.1
5	1	52.5	70.1±072.1						

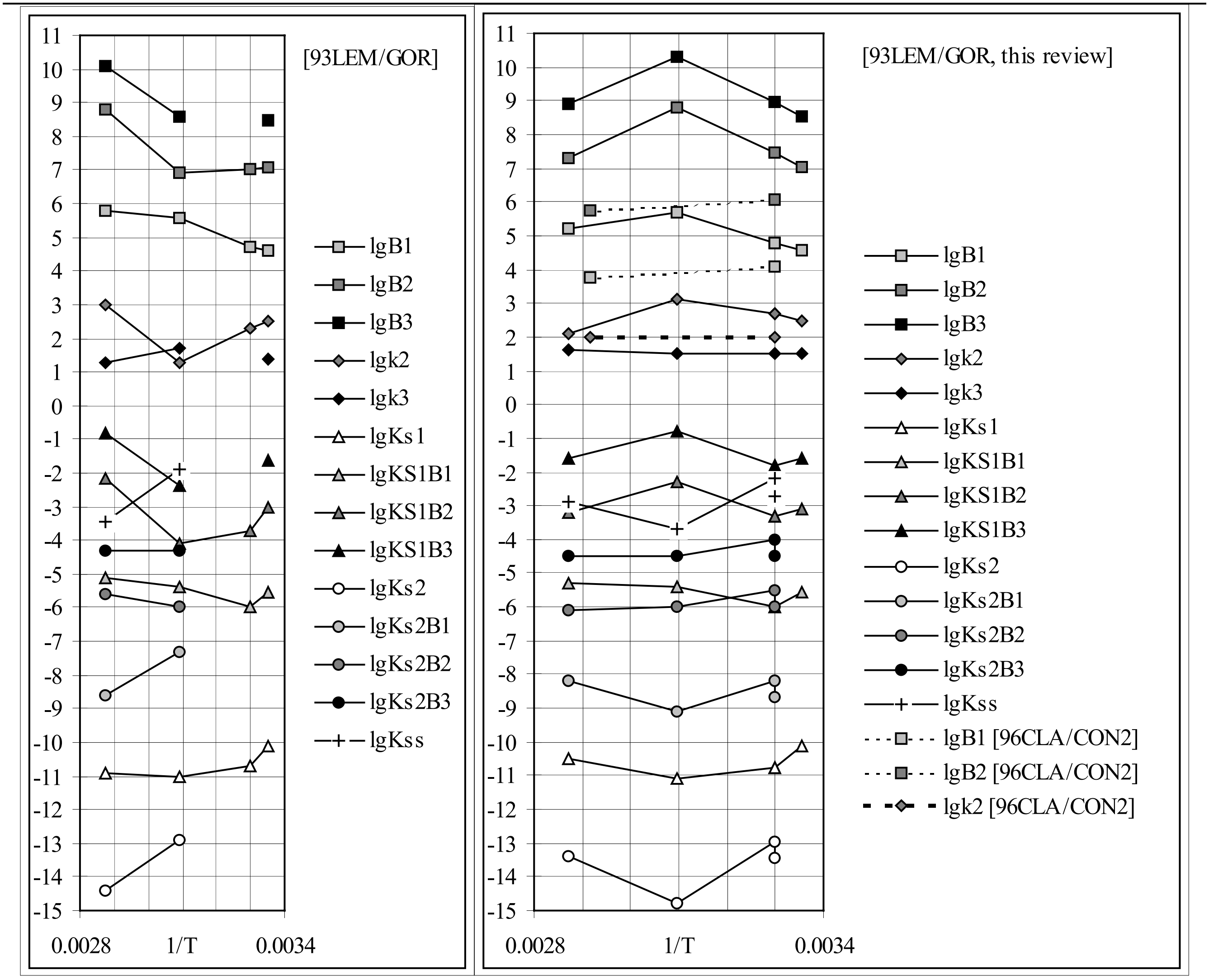


Figure: Temperature influence on equilibrium constant from [93LEM/BOY] solubility measurements.

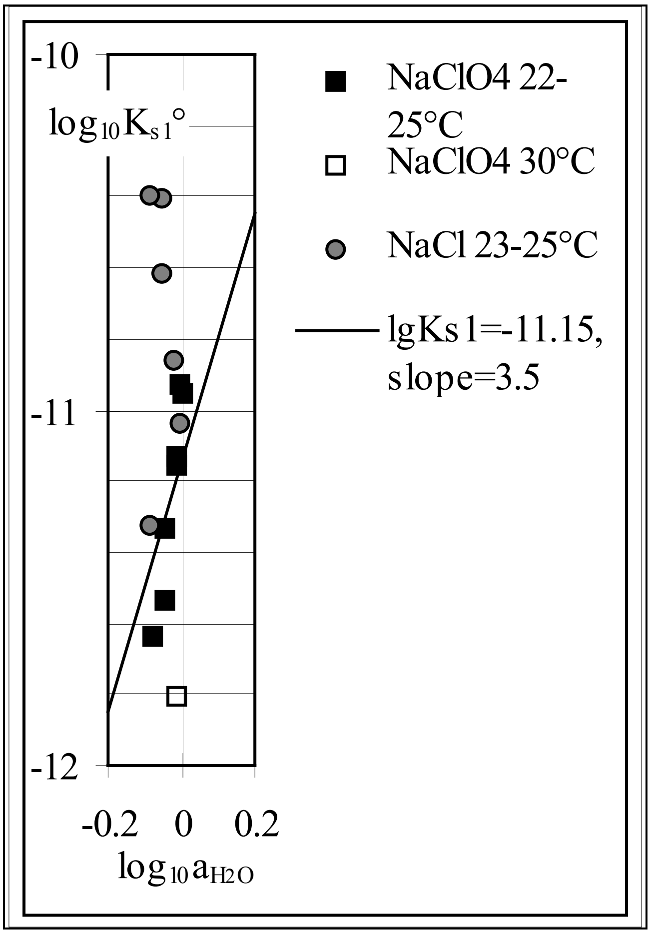


Figure: Influence of water activity, a_{H_2O} on $NaNpO_2CO_{3(s)}$ solubility product, K_{s1}.

Table: Standard complexing constants and SIT coefficients

Data for basic equilibria (used by this review to select thermodynamic data) are tabulated elsewhere, they are not repeated here. The equilibria here tabulated are deduced from the basic equilibria. ε values are deduced from Δε values in the same column, auxiliary data and (when needed) the ε_0 value of the first column (same line). $\beta_i = [NpO_2(CO_3)_i^{1-2i}] /([NpO_2^+] [CO_3^{-2}]^i)$, $k_i = \beta_i / \beta_{i-1}$, $k_1 = \beta_1$. $K_{sj} = [Na^+]^{1-2j} [NpO_2^+] [CO_3^{-2}]^j$ is the solubility product of the $Na_{1-2j}NpO_2(CO_3)_j.x_jH_2O$ compound where x_j values are not clearly established (see the text). $K_{sj,i} = K_{sj}\ \beta_i$, $K_{ss} = K_{s3} / K_{s1} = K_{s3,i} / K_{s1,i}$. $\varepsilon_0 = \varepsilon(NpO_2^+,ClO_4^-)$, $\varepsilon_i = \varepsilon(Na^+,NpO_2(CO_3)_i^{1-2i})$, $\Delta\varepsilon'_i = \varepsilon_i - \varepsilon_0 - i\ \varepsilon(Na^+,CO_3^{-2})$ corresponds to β_i. $\Delta\varepsilon_i = \Delta\varepsilon'_i - \Delta\varepsilon'_{i-1}$ corresponds to k_i, $\Delta\varepsilon_{sj} = (1-2j)\ \varepsilon(Na^+,ClO_4^-) + \varepsilon(NpO_2^+,ClO_4^-) + j\ \varepsilon(Na^+,CO_3^{-2}) + x_j\ r$ (where r is a_{H2O}/m mean value) corresponds to K_{sj}, $\Delta\varepsilon_{sj,i} = \Delta\varepsilon_{sj} + \Delta\varepsilon'_i = (1-2j)\ \varepsilon(Na^+,ClO_4^-) + \varepsilon(Na^+,NpO_2(CO_3)_i^{1-2i}) + (j-i)\ \varepsilon(Na^+,CO_3^{-2}) + x_j\ r$ and $\Delta\varepsilon'_{sj,i} = \varepsilon(Na^+,NpO_2(CO_3)_i^{1-2i}) + (j-i)\ \varepsilon(Na^+,CO_3^{-2})$. $\Delta\varepsilon_{sj,i}$ and $\Delta\varepsilon'_{sj,i}$ both correspond to $K_{sj,i}$; but in the later case water activity and $\varepsilon(Na^+,X^-)$ contribution were subtracted prior to SIT regression, in this way $K_{sj,i}$ data in different Na_zX media were used together for extrapolation to zero ionic strength ($X^z = ClO_4^-$, CO_3^{-2} or Cl^-). In the same way for K_{ss}, $\Delta\varepsilon'_{ss} = \Delta\varepsilon'_{s2} - \Delta\varepsilon'_{s1} = 0$. For $\Delta\varepsilon_{sj}$ $x_1 = 3.5$ and $x_2 = 0$ are used. The references are [1] for [83MAY, 86GRE/ROB], [2] for [89RIG], [3] for [90NIT/STA], [4a] for [91KIM/KLE], [4b] for [94NEC/RUN], [4c] for [95FAN/NEC, 95NEC/FAN], [4d] for [95NEC/RUN], [4e] for [96RUN/NEU], [5] for [95NOV/ROB] (most of the data of this reference are not in accord with the one selected by this review) as cited in [96RUN/NEU], for [6a] published data selected by this review, [6b] weighted linear regression on the same data as [6a]. References [4] are from the same group of authors.

Ref.		$\log_{10}K_{s1}°$	$\log_{10}K_{s2}°$	$\log_{10}K_{ss}°$	$\log_{10}k_1°$	$\log_{10}K_{s1,1}°$
[1]^1						-5.99_5
[4a]						-5.92 ±0.08
[4b]						-6.19 ±0.17
[4b]^2			-14.26_2			$-5.91_4±0.01_4$
[4b]^1			-14.13_3	-3.30_1		$-5.98_1±0.03_4$
[4b]^4			$-14.14_6±0.26_9$			$-5.87_6±0.10_8$
[4b]^5				$-3.17_2±0.29_9$		$-5.91_6±0.18_5$
[4b]^6			$-14.33_1±0.51_8$	$-3.38_5±1.16_9$		
[4c]^7			-14.32 ±0.15	-3.38 ±0.17		-5.91 ±0.10
[4d]			-14.32 ±0.15	-3.32 ±0.17		
[4e]^7			-14.33	-3.19		-6.09
[6a]^8			**$-14.43_9±2.34_6$**	**$-3.28_9±2.41_9$**		**$-6.20_2±0.59_2$**
[6b]				-3.09±1.89		
Ref.		$\Delta\varepsilon_{s1}$	$\Delta\varepsilon_{s2}$	$\Delta\varepsilon'_{ss}$	$\Delta\varepsilon_1$	$\Delta\varepsilon_{s1,1}$
[1]^1		-0.31_3				0.07_7
[4a]		-0.24 ±0.03				-0.05 ±0.04
[4b]		-0.21 ±0.03				0.09 ±0.05
[4b]^2		$-0.26_0±0.06_1$	-0.28_5			$-0.04_4±0.00_7$
[4b]^1		$-0.25_7±0.05_6$	-0.43_1	-0.09_0		$-0.02_0±0.01_8$
[4b]^4		$-0.26_0±0.02_4$	$-0.35_3±0.07_7$			$-0.08_2±0.03_6$
[4b]^5		$-0.26_0±0.02_2$		$-0.16_6±0.08_6$		$-0.08_5±0.06_1$
[4b]^6			$-0.24_3±0.13_1$	$-0.03_9±0.29_6$		
[4d]		-0.22 ±0.03	-0.24 ±0.08			
[4e]^7		0.03 ±0.05	0.06 ±0.07			-0.01 ±0.09
[5]^7		0.07 ±0.09	0.09 ±0.11			0.01 ±0.09
[6a]^8		**$-0.12_8±0.06_0$**	**$-0.12_0±0.08_4$**	**0 ±0.12_1**		**$0.27_0±0.16_6$**
Ref.	ε_0	ε_0	ε_0	0	ε_1	ε_1
[1]^1	0.25 ±0.05	0.43_8			-0.22_1	-0.03_3
[2]^2	0.25 ±0.05				$-0.15_8±0.10_2$	
[2]^1	0.25 ±0.05	0.25 ±0.05				
[4a]	0.25 ±0.05	0.36 ±0.04			-0.02 ±0.07	0.09 ±0.04
[4b]	0.25 ±0.05	0.33 ±0.04			-0.13 ±0.07	-0.05 ±0.05
[4b]^2	0.25 ±0.05	$0.38_4±0.06_9$	0.41_5		$-0.04_6±0.07_9$	$0.08_8±0.01_3$
[4b]^1	0.25 ±0.05	$0.38_1±0.06_5$	0.56_1		$-0.07_1±0.09_3$	$0.06_4±0.02_1$
[4b]^4	0.25 ±0.05	$0.38_4±0.04_0$	$0.48_3±0.10_2$		$-0.00_8±0.07_1$	$0.12_7±0.03_7$
[4b]^5	0.25 ±0.05	$0.38_5±0.03_9$			$-0.00_6±0.08_8$	$0.13_0±0.06_2$
[4b]^6	0.25 ±0.05		$0.37_3±0.14_7$			
[4c]^7	0.25 ±0.05				0.06 ±0.00	
[4d]		0.34 ±0.04	0.37 ±0.10			
[4e]^7	0.19 ±0.02				0.06 ±0.08	
[5]^7	0.22 ±0.08				0.09 ±0.08	
[6]	0.25 ±0.05					
[6a]^8	**0.25 ±0.05**	**$0.25_2±0.06_8$**	**$0.25_0±0.10_7$**		**$-0.22_6±0.16_6$**	**$-0.22_6±0.16_6$**

Ref.	$\log_{10}k_2$	$\log_{10}\beta_2^\circ$	$\log_{10}K_{s1,2}^\circ$	$\log_{10}k_3$	$\log_{10}\beta_3^\circ$	$\log_{10}K_{s1,3}^\circ$	$\log_{10}K_{s2,3}^\circ$
[1][1]		6.41_4	-4.50_4		5.25_7	-5.70_4	
[2][2]		$6.19_9\pm0.13_0$			5.27_0		
[4a]		6.59 ± 0.09	-4.37 ± 0.10		5.73 ± 0.17	-5.23 ± 0.18	
[4b]		6.55 ± 0.23	-4.45 ± 0.24		5.54 ± 0.09	-5.46 ± 0.11	
[4b][2]		$6.57_1\pm0.03_4$	$-4.37_2\pm0.08_1$			-5.37_9	
[4b][1]		$6.56_8\pm0.05_7$	$-4.38_2\pm0.04_8$		5.66_7	-5.36_4	
[4b][4]		$6.60_2\pm0.09_1$	$-4.34_0\pm0.10_3$			$-5.26_6\pm0.26_2$	
[4b][5]		$6.59_6\pm0.08_5$	$-4.35_1\pm0.09_2$		$5.71_8\pm0.119$	$-5.27_2\pm0.21_4$	
[4b][6]						$-5.19_7\pm0.43_0$	
[4c][7]		6.47 ± 0.14	-4.47 ± 0.16		5.37 ± 0.36	-5.57 ± 0.37	
[4d]							
[4e][7]		6.49	-4.65		5.43	-5.72	
[5][7]		5.81			5.19		
[6]		$6.52_6\pm0.13_7$			$5.55_2\pm0.366$		
[6a][8]		**$6.51_7\pm0.19_4$**	**$-4.63_3\pm0.60_0$**		**$5.47_9\pm0.23_9$**	**$-5.67_1\pm0.61_2$**	
[6b]		6.54 ± 0.12			5.62 ± 0.27		

Ref.	$\Delta\varepsilon_2$	$\Delta\varepsilon'_2$	$\Delta\varepsilon'_{s1,2}$	$\Delta\varepsilon'_3$	$\Delta\varepsilon'_3$	$\Delta\varepsilon'_{s1,3}$	$\Delta\varepsilon'_{s2,3}$
[1][1]		0.56_0	0.15_0		0.72_7	0.37_0	
[2][2]		$0.40_5\pm0.09_6$			0.69_5		
[4a]		0.28 ± 0.04	0.04 ± 0.05		0.39 ± 0.07	0.15 ± 0.08	
[4b]		0.35 ± 0.06	0.14 ± 0.07		0.46 ± 0.03	0.25 ± 0.04	
[4b][2]		$0.32_2\pm0.01_8$	$0.01_8\pm0.04_3$			0.21_8	0.23_3
[4b][1]		$0.32_4\pm0.03_0$	$0.02_3\pm0.02_6$		0.48_3	0.21_3	0.25_7
[4b][4]		$0.29_1\pm0.03_0$	$-0.01_4\pm0.03_4$			$0.15_2\pm0.07_5$	$0.12_0\pm0.12_7$
[4b][5]		$0.29_7\pm0.02_8$	$-0.00_8\pm0.03_0$		$0.45_3\pm0.03_4$	$0.15_9\pm0.06_1$	$0.22_3\pm0.23_7$
[4b][6]						$0.11_4\pm0.10_9$	$0.18_3\pm0.15_5$
[4e][7]		-0.08 ± 0.35	0.11 ± 0.29		-0.63 ± 0.78	0.66 ± 0.76	0.69 ± 0.76
[5][7]		0.01 ± 0.57	0.05 ± 0.50		-0.72 ± 0.91	0.79 ± 0.88	0.81 ± 0.88
[6]		$0.51_6\pm0.07_5$			$0.61_2\pm0.19_6$		
[6a][8]		**$0.48_2\pm0.16_3$**	**$0.31_2\pm0.18_4$**		**$0.63_8\pm0.18_0$**	**$0.46_8\pm0.21_6$**	**$0.54_8\pm0.21_0$**
[6b]		-0.51 ± 0.09			-0.58 ± 0.19		

Ref.	ε_2	ε_2	ε_2	ε_3	ε_3	ε_3	ε_3
[1][1]	-0.41_8	-0.47_0	-0.09_8	-0.71_7	-0.71_7	-0.53_0	
[2][2]	$-0.27_3\pm0.11_4$	$-0.31_5\pm0.12_4$		$-0.61_2\pm0.133$	-0.68_5		
[4a]	-0.19 ± 0.10	-0.19 ± 0.09	-0.12 ± 0.06	-0.38 ± 0.14	-0.38 ± 0.12	-0.31 ± 0.10	
[4b]	-0.26 ± 0.11	-0.26 ± 0.10	-0.22 ± 0.07	-0.45 ± 0.15	-0.45 ± 0.11	-0.41 ± 0.07	
[4b][2]		$-0.23_2\pm0.08_0$	$-0.09_8\pm0.053$	-0.381		-0.37_8	-0.31_3
[4b][1]	$-0.23_8\pm0.11_5$	$-0.23_4\pm0.08_4$	$-0.10_3\pm0.040$	-0.493	-0.47_3	-0.37_3	-0.33_7
[4b][4]		$-0.20_1\pm0.08_4$	$-0.06_6\pm0.045$			$-0.31_2\pm0.09_6$	$-0.20_0\pm0.13_1$
[4b][5]	$-0.20_7\pm0.10_9$	$-0.20_7\pm0.08_3$	$-0.07_2\pm0.043$	$-0.45_8\pm0.128$	$-0.44_3\pm0.10_8$	$-0.31_9\pm0.08_6$	$-0.30_3\pm0.23_9$
[4b][6]						$-0.27_4\pm0.12_4$	$-0.26_3\pm0.15_8$
[4c][7]	0.12 ± 0.30			1.29 ± 0.54			
[4e][7]	0.11 ± 0.29			0.58 ± 0.76			
[5][7]	0.05 ± 0.49			0.70 ± 0.88			
[6]		$-0.42_6\pm0.10_8$			$-0.60_2\pm0.22_1$		
[6a][8]	**$-0.39_2\pm0.18_1$**	**$-0.39_2\pm0.18_1$**	**$-0.39_2\pm0.186$**	**$-0.62_8\pm0.208$**	**$-0.62_8\pm0.20_8$**	**$-0.62_8\pm0.22_4$**	**$-0.62_8\pm0.21_2$**

[1] Experimental data were re-evaluated by this review, and[2]. [2] Extrapolation to I=0 was performed by this review. [3] Including data published by other authors. [4] Including data in5 M $NaClO_4$ and[2 and 3]. [5] = [4] and[1]. [6] = [5] including data in 5 M NaCl. [7] Pitzer's equation was used by the author for extrapolation to I = 0, this review calculated ε values from the Pitzer's parameters, the uncertainty is estimated as the difference in ε values between 0.5 and 4 $kg.mol.^{-1}$. [8] Data proposed by this review.

Np(V) hydrolysis.

This part on Np(V) hydrolysis is not a draft for the TDB review.

Table: Published Np(V) hydrolysis constants. For the species $NpO_2(OH)_i$ $K = {}^*\beta_i = [NpO_2(OH)_i]\ [H^+]^i / [NpO_2^+]$, for $NpO_2OH_{(s)}$ $K = {}^*K_{s0}$, ${}^*K_{si} = [Na^+]^i\ [H^+]^{1+i} / [NpO_2^+]$ is $Na_iNpO_2(OH)_{i+1(s)}$ solubility product, ${}^*k_{si} = K_{si} / K_{si-1}$.

Ref	method	medium (M)	T (°C)	species	$\log_{10}K$	this review	$\log_{10}K$
[48KRA/NEL]	pot	0.1 Cl^-, 0.00032 Np		$NpO_2OH_{(aq)}$	-8.9 ± 0.1		<-8.9
				$NpO_2OH_{(s)}$	4.8 ± 0.3		4.8 ± 0.5
[49LAC/MAG]	sol	2.2 NaOH,	?				$\log_{10}{}^*K_{s1}{}^*\beta_2$
		1 Na_2SO_4				$NaNpO_2(OH)_{2(s)}$	> -4.2
						, NpO_2OH^{2-}	
[71MOS3]	sol.	diluted	?	$NpO_2OH_{(s)}$	4.97 ± 0.07		5.0 ± 0.3
				$NpO_2OH_{(aq)}$	-10.1		<-10
				NpO_2^+			
[76SEV/KHA]	pot	0.02 HNO_3	23	$NpO_2OH°$	-8.92 ± 0.04		<-8.9
	spect		20		-8.90 ± 0.10	$NpO_2CO_3^-$?	
	pot	0.02 $HClO_4$	23		-8.84 ±0.05		<-8.8
	sol	diluted HNO_3	?	$NpO_2OH_{(s)}$	5.08 ± 0.04		5.1 ± 0.3
	el.mig			anionic	$pH_{1/2} = 10$		
[78MUS]	sol	NaOH + ?, I = 9	?	$NpO_20H_{(s)}$	3.8		3.86 ± 0.06
[80SCH/GOR]	p.rad	0.01 EtOH	25	$NpO_2OH°$	-8.7 + 1, -0.5		
				$Np(OH)_2^{2+}$		$NpO_2OH_{(s)}$	
				$NpOH^{3+}$		Np(IV)	
[84VIS/VOL]	sol	0.02 to 2.1 NaOH	20	$NpO_2OH_{(s)}$			
			25	$NaNpO_2(OH)_{2(s)}$		$\log_{10}{}^*k_{s1}$	13.4 ± 1.1
		15.0 NaOH		$Na_2NpO_2(OH)_{3(s)}$		$\log_{10}{}^*k_{s2}$	15.5 ± 1.5
		3.5 KOH		$KNpO_2(OH)_{2(s)}$		$\log_{10}{}^*k_{s1}$	13.6 ± 1.2
		9 KOH		$K_2NpO_2(OH)_{3(s)}$		$\log_{10}{}^*k_{s2}$	15.5 ± 1.3
		2 LiOH		$Li_2NpO_2(OH)_{3(s)}$		$\log_{10}{}^*K_{s2}$-lg${}^*K_{so}$	13.8 ± 1.1
[85EWA/HOW]	sol	0 to 0.1 NaOH	?	$NpO_2OH_{(s)}$			4.6 ± 0.4
				NpO_2^+			
[85LIE/TRE]	sol	1 $NaClO_4$	?	$NpO_2OH_{(s)}$	5.19 ± 0.05		5.0 ± 0.3
				NpO_2^+			
				$NpO_2OH_{(aq)}$	-11.7 ± 0.62		<-11.3
				NpO_2OH^{2-}	-23.11 ± 0.05		<-22.6
[87ROE/MIL]	el.mig	$NaClO_4$	25	NpO_2^+			
		0.1		$NpO_2OH_{(aq)}$	-10.45 ± 0.25		
				$NpO_2(OH)_2^-$	-21.95 ± 0.35		
[88NAK/ARI]	sol	0.01 $NaNO_3$	?	NpO_2^+		NpO_2^+	
				$NpO_2OH_{(s)}$	3.3	$NpO_2OH_{(s)}$	3.3 ± 0.5
				$NpO_2OH_{(aq)}$	8.3	CO_3 complexes.	
				NpO_2OH^{2-}	19.4		

[48KRA/NEL]

Kraus, K.A., Nelson, F. *The hydrolytic behavior of uranium and the transuranic elements*, Report AECD-1864, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA, 1948, 12p.

In this work, Np(V) was titrated with NaOH and back titrated in carbon free atmosphere at constant ionic strength. There are no details about glass electrode calibration. When $[Np]_{total} = 0.32$ or 0.89 mM, a buffering region was found at pH about 8.8, while for $[Np]_{total} = 2.0$ and 9.0 mM, the buffering region decreases to pH = 8.0 and 7.3 respectively: this should probably be attributed to precipitation. The stoichiometry of the Np(V) hydroxide formed during these titrations was 1:1 only for the experiment at the highest $[Np]_{total}$. Species with higher OH / Np ratio were formed at higher pH. The author interpreted their results with $NpO_2OH_{(s)}$ precipitation:

$$NpO_2^+ + OH^- \Leftrightarrow NpO_2OH_{(s)}$$

and $NpO_2OH_{(aq)}$ formation:

$$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH_{(aq)} + H^+$$

He determined $\log_{10}K_{s,o} = -9.2 \pm 0.3$ probably in 0.1 M Cl^- solution and $\log_{10}{}^*K_1 = 8.9 \pm 0.1$ respectively. Hence for

$$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH_{(s)} + H^+$$

$\log_{10}{}^*K_{s,0} = 4.8 \pm 0.3$ assuming that the author has calculated $K_{s,o}$ from pH measurements using $K_w = -14.00$. Solubility product value is consistent with later work [76SEV/KHA] [85LIE/TRE] [88TUK/NIT] : the buffering effect was probably mainly due to this solid, ${}^*K_1$ determination is then not much reliable.

[71MOS3]

Moskvin A.I. *Hydrolytic behavior of neptunium(IV, V, VI).* Radiokhimiya, 13 (5) (1971) 681-688, in Russian; Engl. transl.: Sov. Radiochem., 13 (5) (1971) 700-705.

Np(V) solubility measurements in a narrow pH domain (6.5<pH<6.7) at low ionic strength were interpreted with the following equilibrium :

$NpO_2^+ + OH^- \Leftrightarrow NpO_2OH_{(s)}$

$NpO_2OH_{(s)}$ solubility product was calculated : $\log_{10}K_{s,o} = -9.03 \pm 0.07$. Hence for

$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH_{(s)} + H^+$

$\log_{10}{}^*Ks_o = 4.97 \pm -0.07$ assuming that the author has calculated $K_{s,o}$ from pH measurements using $K_w = -14.00$. The experimental results do not deviate much from other similar studies [76SEV/KHA] [85LIE/TRE]; but, there is no indication about the pH electrode calibration. The author also used one other solubility measurement at pH = 8.6, to estimate the $NpO_2OH_{(aq)}$ formation constant:

$NpO_2^+ + OH^- \Leftrightarrow NpO_2OH_{(aq)}$

$\log_{10}K_1 = 3.9$, hence for:

$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH_{(aq)} + H^+$

$\log_{10}{}^*K_1 = -10.1$

but for this determination the pH domain was too narrow to rely on this interpretation. Anyhow by using the numerical values proposed by Moskvin's, one calculates that $[NpO_2OH_{(aq)}]$ was contributing only to a few per cents of the solubility, which is certainly less than the experimental accuracy.

[73SIM/MAT]

Simakin, G.A., Matyashchuk, I.V., Vladimirova, N.A *Potential of the couple Np(VI)-Np(V) in sodium hydroxide solutions,* Sov. Radiochem., 15(1) (1973) 96-98.

Np(VI)/Np(V) electro oxidation and reduction were found to be reversible for coulometry on a platinum electrode in concentrated NaOH solutions. It seems that carbonic gas could not penetrate into the solutions. The junction potential was not measured and the ionic strength was not constant. [NaOH] increase lead to Np(VI) stabilisation : -0.146 V per unit $\log_{10}$[NaOH] when 0.1<[NaOH]<1 M, and about 0 V / $\log_{10}$ unit when 1<[NaOH]<10 M. This work does not seem to be consistent with later works [74PER/ALE] [82PER/SPI].

[74PER/ALE]

Peretrukhin, V.F., Alekseeva, D.P. *Polarographic properties of higher oxidation states of neptunium in aqueous alkaline media*, Sov. Radiochem., 16(6) (1974) 816-822.

Cyclic voltametric studies of Np(VI) in concentrated NaOH solutions (1 to 10 M) pointed out Np(VI) stabilisation : -60 mV/$\log_{10}$[NaOH] up to 5 M (NaOH), -120 mV/lg[NaOH] from 6 to 8.1 M. Assuming that in these conditions Np(V) major species is $NpO_2(OH)_2^-$ and, as for U(VI), Np(VI) major species in 1 M NaOH is $(NpO_2)_3(OH)_7^-$, the expected slope (at constant ionic strength) is much lower (-20 mV/lg[NaOH]). The experimental slopes are not very accurate, and they should be corrected for ionic strength and junction potential variations. The activity coefficients proposed in this review indicate, that ionic strength correction should be too small to explain the discrepancies between the observed and expected slopes. There is no way to estimate the junction potential variations in that work it is then not clear whether the stoichiometry of the limiting hydroxide complexes of actinide(V) and (VI) used in this review can explain this experimental work, or not. On the other end, the Np(VI)/Np(V) formal potential measured here is not consistent with later work by one of the author [82PER/SPI].

[76SEV/KHA]

Sevostyanova, E.P., Khalturin, G.V. *Hydrolytic behavior of neptunium(V)*, Sov. Radiochem., 6 (1976) 738-743.

Np(V) potentiometric titration at low ionic strength (0.02M) with NaOH solution was interpreted with the following equilibrium.

$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH_{(aq)} + H^+$

and the author calculated $\log_{10}{}^*K_1 = -8.92 \pm -0.04$ in HNO_3, -8.84 ± 0.05 in $HClO_4$, but the experiments showed precipitation at about pH = 7.5. The author deduced for the following equilibrium

$NpO_2^+ + OH^- \Leftrightarrow NpO_2OH_{(s)}$

$\log_{10}K_{s,0} = -9.74 \pm -0.10$ in (probably diluted) HNO_3 solution. Assuming that the author have calculated $K_{s,0}$ from pH measurements using $K_w = -14.00$, this corresponds, for the following equilibrium

$NpO_2^+ + H_2O \Leftrightarrow NpO_2OH_{(s)} + H^+$

to $\log_{10}{}^*K_{s,0} = 5.08$. The buffering effect during the titrations (where $[Np(V)]_t$=10.68 mM) was then mainly due to $NpO_2OH_{(s)}$ precipitation and not to $NpO_2OH_{(aq)}$ formation, it was then not consistent to compute ${}^*K_1$ from potentiometric titration (as did the authors).

During the titration, a second pH increase was observed at about pH = 11 for about $[Np(V)]_{total}/[OH]_{added} = 2$. The authors tentatively attributed this pH variation to $NaNpO_{3(s)}$ (= $NaNpO_2(OH)_{2(s)}$ - H_2O) precipitation ; but this is not consistent with their electromigration work and with the shape of their potentiometric titration curve in this pH domain.

The ionic strength was not very constant during the titration. Argon was used to avoid $OH+CO_{2(g)}$ reaction. There is no indication about the pH electrode calibration; quantitative interpretation cannot then be very accurate, and anyhow equilibrium was probably not achieved due to $NpO_2OH_{(s)}$ during the part of the titration where NpO_2OH(aq) was supposed to be formed.

The pH domain (6.6 to 7.7) from which solubility is calculated is not much consistent with the interpretation of the potentiometric and spectrophotometric results. The author also used, absorption spectra to measure $\lg{}^*K_1 = -8.90 \pm 0.10$ in HNO_3 (I=0.001) and -8.89 ± 0.07 $HClO_4$ (I=0.002) solutions where $[Np(V)]_t$=0.07173 mM. The solution was then slightly oversaturated during this experiment. It is not clear whether the authors have avoided the penetration of carbonic gas (from the air): $NpO_2CO_3^-$ species have the same absorption band [89RIG] as the one attributed to NpO_2OH. A careful examination of the spectra (not all of them are given) seems to indicate that more than one complex was formed, the isobestic point should then be less precise than shown ; we reinterpreted the spectrophotometric work using the absorbance at 960 nm (where there is no peak) as base line : either $NpO_2OH°$ (lg^*K_1=-8.8 ± 0.2) or $NpO_2(OH)_2^-$ (lg^*K_2=-17.5 ± 0.4) can be used to fit the results, these values lead to Np(V) hydroxo soluble complexes stability much too stable [85LIE/TRE] : $NpO_2CO_3^-$ formation should then have been the predominant chemical species.

An electromigration study lead to the same conclusion as [69COH/FRI] at pH>10, while at pH<8 Np cationic species was detected at the cathode.

[77MUS]

Musikas C. *Contribution à la chimie de coordination des ions 5f penta, hexa et heptavalents.* Thèse de doctorat es-sciences 10/06/1977. Université Paris 11. see also [78MUS].

$NpO_2OH_{(s)}$ solubility product was measured in an unknown medium (I = 9 M) at 6.4<pH<7.4, lg K_{so}=-10.2, assuming that the author have calculated K_{so} from pH measurements using $\log_{10}K_w$ = -14.0, $\log_{10}{}^*K_{(so)}$ = 3.8, we recalculated from the figure 12 of this thesis, $\log_{10}{}^*K_{(so)}$ = 3.86 ± 0.06. The measured solubilities are a little smaller than other published ones [71MOS3] [76SEV/KHA] [81LIE/TRE] [88TUK/NIT] which could be du to ionic strength effects or glass electrode calibration (there are no indication about this later point). The author noticed that the plot of $\log_{10}$(solubility) vs. pH was a straight line which slope is -1, he deduced that there was no polynuclear soluble complexes; but it is well known that polynuclearity can never be deduced from only solubility measurements controlled by a single solid phase (any polynuclear complex with charge +1, $(NpO_2)_p(OH)_{p-1}^+$ would lead to the same result) anyhow the major soluble species was indeed NpO_2^+ and it was verified that the main hydrolysis reaction was $NpO_2OH_{(s)}$ solid formation.

At pH more than 10, the overall [OH]/[Np] ratio is more than 1 and less than 2: it is not possible to know whether soluble or solid species were formed and whether equilibrium conditions were achieved.

To study Np(V) hydrolysis in more alkaline media, tetra methyl ammonium hydroxide solutions were used. This was a good idea to avoid (with TMA big cation) $NaNpO_2(OH)_{2(s)}$ precipitation [84VIS/VOL] (or eventually soluble Np(V)-Na-OH species formation). Np(V) absorption characteristic pieak at 1016 nm is shown (figure 13 of the thesis) in 0.53, 1.05 and 1.99 M TMAOH solutions, which is not much consistent with a previous work [69COH/FRI] in 1 M TMAOH. Overall molar absorptivity (figure 13 of the publication) was probably a little lower than 10 l/mole in the 0.53 M solution, and lees than 100 l/mole in the more concentrated solutions. This is in consistent with the experimental results given by the author (Tableau X of the publication): measured molar aborbance at 1016 nm for 0.13 < [TMAOH] < 1.99 and 0.74 < [Np(V] < 9.35 (mM?), decreased with increasing basicity; but in 12 M TMAOH solution, molar absorptivity (100 l/mole) was again higher than in 1 M TMAOH, while in 8 M KOH solutions, molar absorptivity was less than 13 l/mole (the molar absorpivity in 0.1 M TMAOH solution is 100 l/mole). There are not enough results in concentrated (>2 M) OH solution to find if they are consistent (or due to any complexing impurities). Aborbance results in TMAOH < 2 M aqueous solutions indicate that there was at least 2 complexes in these conditions. The molar aborbance vs. $[OH^-]$ curves are shifted toward higher $[OH^-]$ when [Np(V] increases which suggests that (at least) the complex(s) in less alkaline medium is (are) polynuclear(s). The author had noticed the [Np(V)] dependence of Np(V) molar absorptivity, he also proposed polynuclearity but only in the most alkaline conditions. It is the only work that reports such an intense and relatively broad Np(V) absorption pieak at 1016 nm. It would be very surprising that the pieak at 1016 nm would be du to a known Np(V)-OH-CO_3 complex [84VAR/BEG, [89RIG]. There are not enough results to verify internal consistency of the data of this work.

[80SCH/GOR]

Schmidt, K.H., Gordon, S., Thompson, R.C., Sullivan, J.C. *A pulse radiolysis study of the reduction of neptunium(V) by the hydrated electron*, J. Inorg. Nucl. Chem., 42 (1980) 611-615.

The pulse radiolysis technique was used on 10 mM EtOH, 0.5 mM NpO_2ClO_4 aqueous solutions at pH 3 to 7. In this medium, NpO_2^+ is reduced (by radiolysis products) to Np(IV) which rearranges to stable hydrolysis species: a 0.4 µs long, electron pulse was detected by a sharp increase of the conductivity that lasted a few µs and finally decreased to an asymptotique negative value that was observed during typically 100 µs. The author proposed an interpretation that used independently and previously measured parameters and finally lead to fit 2 hydrolysis constants to the variation of the asymptotique conductivity, against pH. The 2 fitted parameters are the Np(V) first hydrolysis constant, $^*K_1$(V), and the Np(IV) stepwise second hydrolysis constant, $^*k_2$(IV). According to [85LIE/TRE] $NpO_2OH_{(s)}$ precipitation in a 0.5 mM NpO_2^+ I = 1 M ($NaClO_4$) solution begins at pH=8.3. Difference in ionic strength and in pH electrode calibration (that are not much described in both publications) are not enough to assume that the main Np(V) hydrolysis reaction during the pulse radiolysis measurements were not $NpO_2OH_{(s)}$ precipitation. Asymptotic conductivities is supposed to be always negative, but one figure showed it positive (this could be a typographic error), anyhow it is clear that the absolute value of the signal (used to fit the 2 hydrolysis constants) go down to 0 at pH>7 which is also consistent with $NpO_2OH_{(s)}$ precipitation. Beside the precipitation problem, it is difficult to understand why blank conductivity measurements (in Np(V) solutions at different pH and without radiolysis) were not reported: this should had validated the author interpretation by producing independent information about Np(V) hydrolysis (that occurs before and during radiolysis); pulse radiolysis could then essentially produce information about first steps (during 100 µs) of Np(V) reduction and Np(IV) hydrolysis; information about the total Np(IV) concentration generated (during this 100 µs) and its variations might also be useful to detect polymerisation (or to verify that it is negligible).

[82PER/SPI]

Peretrukhin, V.F., Spitsyn, V.I. *Spectrochemical determination of the oxidation potentials and the thermodynamic stability of the valence states of the transuranium elements in aqueous solution*, Bull. Acad. Sci. USSR, Chem. Sci., 31 (1982) 726-730.

Np(VI)/Np(V) redox potential was found do be constant in 1 to 15 M NaOH solutions. This does not agree with a previous work by one of the author.[74PER/ALE].

[84VIS/VOL]

Visyashcheva, G.I., Volkov, Y.F., Simakin, G.A., Kapshukov, I.I. *Some hydroxides of pentavalent neptunium*, Sov. Radiochem., 26(2) (1984) 156-160.

$MNpO_2(OH)_{2(s)}$,nH_20 and $M_2NpO_2(OH)_{3(s)}$,nH_20 (M = Li, Na or K) were prepared at room temperature. This review estimated their solubility product from their precipitation conditions. $NpO_2OH_{(s)}$ was prepared in 0.02 M NaOH solution and $NaNpO_2(OH)_{2(s)}$ in 2.1 M. There is a unique NaOH concentration, [NaOH]°, for which both solids precipitate and

$$0.02 < [NaOH]° < 2.1 M;$$

in this condition

$$K_{s1}/K_{so} = [Na^+][OH^-] = 2\ [NaOH]°.$$

The same type of calculation was performed by this review the other solid compounds:

solid	[MOH]° (M)	$\log_{10}$[MOH]°	$\log_{10}K_{si} - \log_{10}K_{si-1} = \log_{10}k_{si}$
$NpO_2OH_{(s)}$	0.02	-1.7	
$NaNpO_2(OH)_{2(s)}$	2.1	0.3	$-1.4 < \log_{10}k_{s1} < 0.6$
$Na_2NpO_2(OH)_{3(s)}$	15.0	1.2	$0.6 < \log_{10}k_{s2} < 1.5$
$KNpO_2(OH)_{2(s)}$	3.5	0.5	$-1.4 < \log_{10}k_{s1} < 0.8$
$K_2NpO_2(OH)_{3(s)}$	9.0	1.0	$0.8 < \log_{10}k_{s2} < 1.3$
$Li_2NpO_2(OH)_{3(s)}$	2.0	0.3	$-1.1 < \log_{10}K_{s2} - \lg K_{so} < 0.9$

[86EWA/HOW]

Ewart, F.T., Howse, R.M., Thomason, H.P., Williams, S.J., Cross, J.E. *The solubility of actinides in the near-field*, Sci. Basis Nucl. Waste Management IX, Mater. Res. Soc. Symp. Proc., 50 (1986) 701-708.

Np(V) solubility was measured in NaOH solutions (the quantity needed to obtain 9.5<pH<13), so ionic strength was varying from 0 to 0.1 M. Np oxidation state was controlled in the mother solution. Equilibration time was only 24 hours, there is no indication about glass electrode calibration. For pH<11.8 experimental results are consistent with other similar work, [71MOS3] [76SEV/KHA] [78MUS] [85LIE/TRE]: solubility was certainly controlled by the $NpO_2OH_{(s)}$ solid phase and NpO_2^+ was the major soluble phase, this review then calculated

$$\lg{}^*K_{so} = 4.6 \pm 0.4 \quad (I = 0 \text{ to } 0.1\ M)$$

At higher pH, solubility is lower than the extrapolation of the above solubility product law and other experimental results at higher ionic strength [85LIE/TRE]. The authors deduced that soluble hydroxo-Np(V) complexes could not be formed for kinetic reasons. This behaviour, in our opinion is not proved and usually occurs only for polynuclear soluble complexes. Such low solubility at pH>12 can be due to experimental artefact such as $Np(OH)_{4(s)}$ precipitation.

[85LIE/TRE]

Lierse, C., Treiber, W., Kim, J.I. *Hydrolysis reactions of neptunium(V)*, Radiochim. Acta, 38 (1985) 27-28.

Np(V) solubility was measured, probably at constant ionic strength, $NaClO_4$ 1 M, and at 6.8 < pH < 13. There is no indication about glass electrode calibration. The authors used filters with different pore sizes (220 down to 1 nm). Only the filter with the smallest pore size lead to slightly lower solubilities at 11.5 < pH < 12.5 but not at 12.5 < pH < 13. As pointed out by the authors, the interpretation of this difference is not clear. This lower solubility is consistent with the data of the [86EWA/HOW] publication, it is then not demonstrated that the scattering of the data is only due to the pore size of the filters. To recalculate the equilibrium constants, this review used the experimental points ($\log_{10}$solubility, pH) from the figure of this publication. This work confirmed [71MOS3] [76SEV/KHA] [86EWA/HOW], that at pH < 11, $NpO_2OH_{(s)}$ solid phase control Np(V) solubility, and that NpO_2^+ is the major soluble species. The Np(V) solubility increase at pH > 11 was attributed to $NpO_2(OH)_2^-$ formation. This is a reasonable assumption; but it was not demonstrated, typically any $(NpO_2)_i(OH)_{i+1}^-$ complex would fit the experimental data as well. If the solution were polluted with carbonate, other complexes could also explain these data. The stoichiometry of the Np(V) soluble hydrolysed species proposed by Lierse was then not established; but it was probably the correct one.

[87ROE/MIL]

Roesch, F., Milanov, M., Hung, T.K., Ludwig, R., Buklanov, G.V., Khalkin, V.A. *Electromigration of carrier-free radionuclides: 5. Ion mobilities and hydrolysis of Np(V) in aqueous perchlorate solutions*, Radiochim. Acta, 42 (1987) 43-46.

Electromigration experiments were performed directly in 0.1 M $NaClO_4$ aqueous solutions. Np(V) hydrolysis constants were deduced. There is no much indication about glass electrode calibration, neither experimental set up to avoid penetration of CO_2 into the solutions. $[NpO_2]_{total}$ was 1 mM, Np(V) should then precipitate at about pH = 8.5 [76SEV/KHA] [85LIE/TRE]; but this was not mentioned in this work. On the other end, the authors verified that the results were not $[Np]_{total}$ dependent (using carrier free ^{239}Np); but not enough details are given to recalculate the influence of various parameters (ionic strength, $[Np]_{total}$, $[Cl^-]$, $[NO_3^-]$) that were varied. Mobility slightly increased around pH = 5, it is not well understood (the authors proposed $NpO_2^+.(H_3O^+)_n$, but this is not much consistent with solubility and spectrophotometric measurements [76SEV/KHA] [85LIE/TRE]. As for solubility measurements [85LIE/TRE] the results at pH > 6 were interpreted with direct NpO_2^+ transformation into $NpO_2(OH)_2^-$.

[88NAK/ARI]

Nakayama, S., Arimoto, H., Yamada, N., Moriyama, H., Higashi, K. *Column experiments on migration behaviour of neptunium(V)*, Radiochim. Acta, 44/45 (1988) 179-182.

Np(V) solubility was measured at different pH. There is no indication about glass electrode calibration. The CO_2 concentration in the solutions was estimated to be less than 0.01 mM; but there are no much indication concerning the experimental procedure to reach this purity neither about the calculations to do this estimation. Redox potential measurements indicate that solutions were equilibrated with the air, it is then not much consistent with low CO_2 concentration in the solutions. Experimental solubility plotted against pH (7 to 12.4) were scattered, and there are practically no pH dependency at $8 < pH < 11.5$. Most of the results are not consistent with previous solubility measurements [76SEV/KHA] [78MUS] [85LIE/TRE]. In our opinion carbonate complexation explains the scattering of the results. Filtration lead to less inconsistent results after at least 1 week equilibration time when colloidal $NpO_2OH_{(s)}$ is dissolved or has grown and also at high pH where probable carbonate complex formation, avoids metastable colloid formation.

Np(VI) en milieu bicarbonate / carbonate oxydante.

Pierre Vitorge, Hélène Capdevila.

Résumé

Simakin (1977) a montré que le complexe limite de Np(VI) est $NpO_2(CO_3)_3^{-4}$ en mesurant le potentiel normal de Np(VI)/Np(V). Ses résultats ont été confirmés par Riglet (1989) puis Offerlé, Capdevila et Vitorge (1995). L'influence de la température mesurée par Ullman et Schreiner (1988), et par Offerlé, Capdevila et Vitorge (1995) permet d'estimer l'enthalpie ou entropie de réaction, voire la capacité calorifique. Grenthe, Riglet et Vitorge (1986 et 1989) ont mis en évidence par spectrophotométrie, l'espèce trinucléaire $(NpO_2)_3(CO_3)_6^{-6}$; ce qui rend partiellement caduque l'interprétation que fait Maya (1984) de ses dosages acido basiques. Réinterprétés, ils confirment la formation de l'espèce trinucléaire et mettent en évidence un complexe mixte polynucléaire, certainement $(NpO_2)_2(OH)_3CO_3^{-1}$ comme Maya l'avait proposé. Quelques données non publiées permettent d'estimer la stabilité des complexes intermédiaires mononucléaires et le produit de solubilité de $NpO_2CO_{3(s)}$. Ceux de $M_4NpO_2(CO_3)_{3(s)}$ ($M^+ = K^+$ ou NH_4^+) sont déduits des mesures de Gorbenko-Germanov et Klimov (1966) et de Moskvin (1975) respectivement interprétées et réinterprétées. Les valeurs standard sont déterminées pour $K°(\log_{10}K°,\Delta\varepsilon) = \beta_3^{VI}/\beta_3^{V}(13{,}87\pm0{,}12,\ 0{,}14\pm0{,}04$ correspondant à $E°_{VI/V} = 0{,}338\pm0{,}006V/SHE)$, $\beta_3(19{,}35\pm0{,}27)$, $\beta_2(16{,}47\pm0{,}58)$, $\beta_1(9{,}10\pm0{,}99)$, $\beta_{3,6}/\beta_3^{3}(8{,}27\pm2{,}35,\ 0{,}49\pm0{,}49)$, $K_{s0}(-14{,}52\pm0{,}43)$, $K_{s4}(-7{,}03\pm1{,}3$ et $-7{,}44\pm1{,}11$ pour K^+ et NH_4^+ respectivement) où $\Delta\varepsilon$ est la différence de coefficient d'interaction spécifique en milieu Na^+ pour calculer l'influence de la force ionique selon la TIS. Pour le complexe limite l'influence de T sur $\Delta\varepsilon$ et ses valeurs en milieux K^+ et NH_4^+ sont également déterminées. Ces valeurs sont en cours de discussion au sein de l'OCDE-AEN-TDB.

Summary

Simakin (1977) proved the Np(VI) limiting complex is $NpO_2(CO_3)_3^{-4}$, by measuring the normal potential of the Np(VI)/Np(V) redox couple. His results were later confirmed by Riglet (1989), and by Offerlé, Capdevila and Vitorge (1995). Temperature influence as studied by Ullman and Schreiner (1988), and by Offerlé, Capdevila and Vitorge (1995) allowed to determine enthalpy or entropy, and even heat capacity changes. Grenthe, Riglet and Vitorge (1986 and 1989) proved the existence of the trinuclear species $(NpO_2)_3(CO_3)_6^{-6}$, by using a spectrophotometric technique. This showed some of Maya's (1984) assumptions to treat his experimental potentiometric data, were in error. This review reinterpreted them to point out the trinuclear species was formed in some of the measurements and to show evidence of a new polynuclear mixed species, certainly $(NpO_2)_2(OH)_3CO_3^{-1}$, as initially proposed by Maya. Unpublished data allowed to estimate the stability of intermediary mononuclear complexes and $NpO_2CO_{3(s)}$ solubility product. $M_4NpO_2(CO_3)_{3(s)}$ ($M^+ = K^+$ or NH_4^+) ones are deduced from Gorbenko-Germanov and Klimov (1966), and Moskvin (1975) data as respectively interpreted and reinterpreted by this review. Standard values are determined for $K°(\log_{10}K°,\Delta\varepsilon) = \beta_3^{VI}/\beta_3^{V}(13.87\pm0.12,\ 0.14\pm0.04$ corresponding to $E°_{VI/V} = 0.338\pm0.006V/SHE)$, $\beta_3(19.35\pm0.27)$, $\beta_2(16.47\pm0.58)$, $\beta_1(9.10\pm0.99)$, $\beta_{3,6}/\beta_3^{3}(8.27\pm2.35,$ $0.49\pm0.49)$, $K_{s0}(-14.52\pm0.43)$, $K_{s4}(-7.03\pm1.3$ and -7.44 ± 1.11 for K^+ and NH_4^+ respectively) where $\Delta\varepsilon$ is specific interaction coefficient change in Na^+ media to estimate activity coefficient by using the SIT formula. For the limiting complex T influence on $\Delta\varepsilon$, and its values in K^+ and NH_4^+ media are also determined. All these numbers are under discussion within OECD-NEA-TDB.

Sommaire

1. Introduction

Cette revue la chimie de Np(VI) est en cours de comparaison avec celle effectuée sur le plutonium par Ullman et Sullivan. Nous donnons ici une version provisoire élaborée pour la TDB (Thermodynamic Data Base de l'AEN OCDE) qui, après corrections, fera partie du volume Chemical thermodynamics of Neptunium and Plutonium. Les notations et méthodologies sont celles de la TDB [92GRE/FUG, 95SIL/BID]. L'appendix A est le résultat de l'analyse de chaque publication. La synthèse fait l'objet du chapitre placé en tête. Nous avons discuté du contenu de ce texte avec Robert Lemire, AECL (Canada) président du groupe de spécialistes du neptunium et du plutonium pour la TDB, et avec William Ullman (Université du Delaware, USA) et James Sullivan (Laboratoire d'Argonne, USA) qui sont chargés d'un travail parallèle sur le plutonium. Nous sommes arrivés à des conclusions convergentes. Ce texte est en anglais pour servir de document de travail au sein de la TDB. Une version corrigée, abrégée et nettement améliorée (notamment en ce qui concerne la langue) par Robert Lemire, est incluse dans le "draft" du 11 Septembre 1997. Les données sélectionnées permettent de rendre compte de l'ensemble des résultats publiés ; mais uniquement certaines d'entre elles ont été utilisées pour cette sélection de données thermodynamiques (les autres comportent trop d'erreurs ou d'incertitudes). Les parties rédigées en anglais (destinées à la TDB) justifient ces appréciations ; je rajoute dans cette introduction quelques appréciations supplémentaires pour donner des indications sur la façon de compléter ces données. Les quelques remarques historiques et mon opinion sur la relativement bonne qualité de certains travaux, sont données dans cet objectif. Avant d'entreprendre la mesure d'une donnée manquante, il est bon en effet de chercher à justifier qu'on sera capable de faire mieux que nos prédécesseurs, il peut alors être utile de prendre exemple ou appui sur les meilleurs travaux et de savoir en particulier si certaines mesures non pas été entreprises ou ont été abandonnées à cause de difficultés expérimentales ou pour d'autres raisons.

Le point de départ de la construction de l'ensemble des données sur Np(VI) en milieu bicarbonate/carbonate, est la détermination de la stabilité du complexe limite, $NpO_2(CO_3)_3^{-4}$. Ce fut l'objet du stage de DEA de Sophie Offerlé [95OFF/CAP]. Elle a mesuré le potentiel normal du couple Np(VI)/Np(V) en fonction de la force ionique et de la température et déterminé ainsi les valeurs standard de Δ_rG, Δ_rS et même Δ_rCp. J'ai revérifié toute l'interprétation à partir des données brutes, Hélène Capdevila l'a indépendamment vérifiée pour finalement trouver pratiquement les mêmes nombres. Pendant sa thèse au laboratoire [89RIG], Chantal Riglet avait également mesuré le potentiel du couple Np(VI)/Np(V) qui s'avère être en parfait accord avec les résultats de Sophie Offerlé. Malgré quelques incertitudes typographiques, il me semble que les résultats de Simakin [77SIM] sont en excellent accord avec les nôtres. Ceci confirme la bonne qualité du DEA de Sophie Offerlé qui n'a pu continuer en thèse uniquement en raison de l'arrêt de ce programme expérimental. La stabilité de complexe limite de Np(VI) se déduit du potentiel du couple Np(VI)/Np(V) en milieu carbonate par un cycle thermodynamique incluant le potentiel de ce couple en milieu non complexant (mesuré au laboratoire par Piotr Robouch et Chantal Riglet [87ROB, 89RIG, 89RIG/ROB]) et la constante de formation du complexe limite de Np(V). C'est cette dernière qui induit l'incertitude numérique la plus importante. Or il serait souhaitable d'obtenir une meilleure précision puisque le complexe limite est lui-même le point de départ pour les données des autres complexes de Np(VI). Pour améliorer la précision, j'espérais m'appuyer sur des mesures de solubilité de Np(VI) car la méthode avait été utilisée au laboratoire par Piotr Robouch pour le plutonium [87ROB, 87ROB/VIT] et que nous étions déjà arrivés à préparer le solide correspondant de Np(VI) [86GRE/ROB]. Ce fut le sujet de stage de DEA de Frédérique Coudray ; il n'a malheureusement pas eu le temps d'obtenir suffisamment de résultats pour les interpréter. J'ai les inclus dans la présente note ("§ Supplementary materials") et suis arrivé à un extraire des constantes de formation possibles que j'ai utilisées en l'absence de meilleures données publiées. Ces constantes sont assez voisines de celles de l'uranium et en accord avec une publiée par Maya (que j'évoque plus bas). Il me semble donc que ces mesures si elles étaient menées à leur terme, permettraient d'obtenir des résultats plus précis. En plus des difficultés propres aux mesures en solution (maîtrise du système carbonate, contrôle des coefficients d'activité et surtout du potentiel de jonction lors de l'étalonnage et de la mesure du pH) et de solubilité (attendre suffisamment longtemps l'équilibre en vérifiant qu'on obtient les mêmes résultats par précipitation et dissolution, caractériser par diffraction de rayons X le solide après -et non uniquement avant- la mise à l'équilibre) pour lesquelles des méthodologies sont données dans les publications citées ici, les simulations que je donne dans cette note montre bien qu'on obtient difficilement l'équilibre entre $NpO_2(CO_3)_3^{-4}$ et $NpO_2CO_{3(s)}$ en raison de la formation du complexe trinucléaire et de la précipitation d'une nouvelle phase solide (peut-être $Na_4NpO_2(CO_3)_{3(s)}$). On peut faire face à ces difficultés en étudiant l'influence de la force ionique et en reproduisant à force ionique plus faible l'étude spectrophotométrique de la dissociation du complexe limite [86GRE/RIG, 89RIG]. L'étude de solubilité donnerait également les coefficients d'activité de NpO_2^{+2} et des complexes mononucléaires intermédiaires, qui ne sont jusqu'à présent estimés que par analogie avec l'uranium.

La venue au laboratoire en année sabbatique du Professeur Ingmar Grenthe (KTH Stockholm) a permis à Chantal Riglet de mettre en évidence l'espèce trinucléaire $(NpO_2)_3(CO_3)_6^{-6}$ [86GRE/RIG, 86GRE/ROB, 89RIG] analogue du complexe d'uranium qu'il avait trouvé précédemment et de celui de plutonium dont il a mesuré la stabilité à cette occasion. Personne n'avait pensé à inclure l'hypothèse de polymérisation dans l'interprétation de ce type de mesures chimiques en solution aqueuse ce qui avait induit la publication de quelques erreurs. Malgré des preuves concordantes et sans ambiguïté de son existence, Ingmar Grenthe avait du mal à faire admettre la formation de l'espèce trinuclaire d'uranium, notamment auprès d'auteurs américains, jusqu'au moment où David Clark (Los Alamos USA) confirmait par RMN et plus tard par EXAFS l'existence de ces complexes trinucléaires. Cela met en évidence deux types de difficultés classiques. Il fallait d'abord bien comprendre et calculer les meilleures conditions chimiques permettant de préparer ces complexes en concentration suffisamment élevée et relativement pures. On utilise d'autre part classiquement des ajustements multiparamétriques des données expérimentales à leurs valeurs théoriques calculées en prenant en compte des complexes de différentes stoechiométries, la stoechiométrie retenue étant celle donnant le meilleur ajustement, c'est-à-dire (en général) minimisant la somme des moindres carrés. Ce critère statistique comporte une part d'arbitraire et ne permet pas de mettre en évidence les erreurs systématiques ou méthodologiques (voir par exemple la discussion de la référence [84MAY] dans l'Appendix A). J'ai proposé une méthode graphique qui donne des résultats bien plus faciles à interpréter (voir la discussion de la référence [89RIG] dans l'Appendix A).

Les mesures de Maya (dosages acido-basiques et potentiel normal apparent du couple Np(VI)Np(V)) sont pour une bonne part en désaccord avec ceux cités ci-dessus ; mais on voit assez facilement (voir la discussion de la référence [84MAY] dans l'Appendix A) que les résultats des deux techniques expérimentales utilisées dans cette publication, ne sont pas vraiment cohérents entre eux sans que l'auteur n'en donne d'explication très convaincante, alors qu'il reconnaît plus ou moins explicitement que le traitement statistique de ses résultats ne lui permet pas vraiment de conclure (ce qui d'ailleurs ne l'a pas empêché de publier dans une revue prestigieuse -Inorg. Chem.-). Alors qu'on invoque la formation de complexes polynucléaires, la concentration totale en Np(VI) utilisée est pratiquement constante. C'est d'autant plus dramatique que deux des complexes importants, $NpO_2(CO_3)_2^{-2}$ et $(NpO_2)_3(CO_3)_6^{-6}$, sont polymères l'un de l'autre ($(NpO_2)_3(CO_3)_6^{-6} \equiv (NpO_2(CO_3)_2^{-2})_3$). La dissociation de $NpO_2(CO_3)_3^{-4}$ par ajout d'acide donne d'abord les complexes $NpO_2(CO_3)_3^{-2}$ et $(NpO_2)_3(CO_3)_6^{-6}$ puis sans doute $(NpO_2)_2(OH)_3CO_3^{-1}$ et enfin de nombreuses autres espèces autour du point équivalent (car le pH y varie brutalement) ; mais il ne faut pas tenir compte de cette fin du dosage car Np(VI) devait être en train de précipiter (sans que l'auteur ne s'en rende compte). Ceci induit un certain bruit statistique. Par ailleurs les conditions chimiques étaient telles que c'est $(NpO_2)_2(OH)_3CO_3^{-1}$ qui prédominait le plus souvent, masquant ainsi l'effet des autres complexes sur la somme des moindres carrés. Quand seules les deux complexes $NpO_2(CO_3)_2^{-2}$ et $(NpO_2)_3(CO_3)_6^{-6}$ prédominent, ils sont en proportions pratiquement constantes (puisque $[Np(VI)]_{total}$ est constant), et le calcul de leur stabilité relative ne peut être qu'un artefact statistique. En fait il y a presque toujours un troisième complexe en début ($NpO_2(CO_3)_3^{-4}$) ou fin ($(NpO_2)_2(OH)_3CO_3^{-1}$) de dosage, dont la formation diminue la concentration totale en Np(VI) disponible pour les complexes de stoechiométrie 2 CO_3 pour 1 Np(VI) et donc déstabilise plus $(NpO_2)_3(CO_3)_6^{-6}$ que $NpO_2(CO_3)_3^{-2}$. Finalement il y a très peu de conditions (seulement trois points expérimentaux) où $(NpO_2)_3(CO_3)_6^{-6}$ est en concentration suffisante pour avoir un effet notable ce qui ne correspond plus au domaine d'utilisation des algorithmes classiques d'ajustement. On pourrait penser améliorer le traitement des résultats simplement en rajoutant des mesures expérimentales à pression partielle de gaz carbonique plus élevées (pour éviter la formation de complexes mixtes) et en faisant varier la concentration totale de Np(VI). Toutefois j'hésiterais à me lancer dans de telles mesures, car les résultats de Chantal Riglet montrent qu'on obtient alors des résultats bien plus concluant en suivant le dosage par spectrophotométrie et qu'on risque de ne rien voir d'autre que le complexe trinucléaire. Enfin, bien que la potentiométrie soit une des méthodes les plus classiques pour déterminer les constantes d'équilibre, l'exemple ci-dessus montre que l'interprétation des résultats n'a rien d'évident.

Remerciements

2. Np(VI) carbonate complexes

2.1. The aqueous neptunium-carbonate system

Studies of the carbonate complexes are not straightforward since the carbonate ion, CO_3^{-2}, is a base, hence hydrolysis including formation of mixed (CO_3^{-2}-OH^-) complexes may occur together with carbonate complexation. In acidic media, the carbonate ion is transformed into carbonic gas, $CO_{2(g)}$. Hence when M_2CO_3 ($M^+ = Na^+$, K^+ or NH_4^+ typically) solution is in contact with air, $\log_{10}P_{CO_2}$ can quickly vary from -7 or -6 to -3.5 (it is not buffered). This typically induces up to nearly seven orders of magnitude shift on the formation constant deduced from redox measurements of the Np(V)/Np(IV) couple. One way to avoid this problem is to work in close batches containing carbonate-bicarbonate buffer. To control (and study) lower concentration of carbonate ion, bicarbonate-carbonic gas buffer is also used; the system cannot be closed: bubbling carbonic gas is used, and the major anion of the carbonate system is then the bicarbonate anion, HCO_3^-. Still the carbonate aqueous system is a two component system: it can be formally described with two species, typically when only OH^- and CO_2 are used to describe the system, HCO_3^- and CO_3^{-2} are formally written $OHCO_2^-$ and $(OH)_2CO_2^{-2}$ respectively. As a consequence when experiments are only performed in equilibrium with air, CO_3^{-2} is equivalent to 2 OH^- and not a unique interpretation can be proposed for such experimental works (typically such methodology cannot make the difference between the transformation of NpO_2^+ into $NpO_2CO_3^-$, or into $NpO_2(OH)_2^-$). This was already explained in this series of reviews for the Uranium-carbonate system [92GRE/FUG] pages 308 and 312: the same observations still stand when studying the Neptunium-carbonate aqueous system, and the same type of methodology was used in the present review.

Some published measurements were performed in concentrated M_2CO_3 or $MHCO_3$ ($M^+ = Na^+$, K^+ or NH_4^+) media without addition of an inert salt. Ionic strength was then dependent on the concentration of reactive species (typically CO_3^{2-}). Junction potential also varied during redox or pH measurements. It was then difficult to deduce quantitative interpretation and accurate thermodynamic data. This review still considered these data since there are too few other experimental results.

Same species (same stoichiometry) with similar formation constant (or solubility product) values are expected within the actinide series. Neptunium is the most stable element at the +5 oxidation state, within the actinide series. Hence there are more published works on Np(V) than on the other actinide(V) elements, and the stoichiometries of actinide(V) species were usually determined from experimental information concerning Np(V): analogy was then used to propose the stoichiometry of Pu(V) species (Chapter VII.6.2) TO BE CHECKED WITH BILL as previously for U(V) [92GRE/FUG]. Conversely Np(IV) and Np(VI) species are expected to be the same as the well-documented corresponding Uranium ones [92GRE/FUG]. There is usually not enough published information to determine the stoichiometry and propose thermodynamic data for all these expected Np(IV) and Np(VI) species: this review then extensively used analogy with Uranium (for specific interaction coefficients of anions with charge -1 to -3, and for stoichiometry) and preferred to propose values with large uncertainty and even possible maximum values, rather than no value at all. In the same way, Np(III) analogy with Am(III) [95SIL/BID] can be used; but usually Np(III) reduces water in conditions where Np(III) carbonate complexes are expected to form.

2.1.1. Np(VI) carbonate complexes

There are several publications on the Neptunium(VI)-carbonate system. The available information is summarised in Table VI.a, where the reinterpretation of the data performed by this review, extrapolation to I = 0, and some experimental information are also given. Details of the selection or reinterpretation of published works are given in the Appendix A. There is correct available experimental information on only two Np(VI) complexes in carbonate/bicarbonate media:

- Simakin experimental study of the Np(VI)/Np(V) redox equilibrium in Na_2CO_3 and K_2CO_3 media [77SIM] was used to proposed the stoichiometry and the formation constant of the limiting complex, $NpO_2(CO_3)_3^{4-}$. It was confirmed later by Riglet [89RIG] and by Offerlé, Capdevila and Vitorge [95OFF/CAP].
- Grenthe, Riglet and Vitorge [86GRE/RIG, 89RIG] showed that, as for Uranium, the limiting complex is dissociated into the trinuclear one $(NpO_2)_3(CO_3)_6^{6-}$ when Np(VI) total concentration is more than 1 mM.

This is not much when comparing with the Uranium thermodynamic data proposed [92GRE/FUG] for $UO_2CO_{3(aq)}$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_2(OH)_3CO_3^-$, $(UO_2)_3O(OH)_2HCO_3^+$ carbonate or mixed hydroxide-carbonate soluble complexes, and for $UO_2CO_{3(s)}$ and $Na_4UO_2(CO_3)_{3(s)}$ solid compounds. From the above Np(VI) starting species several other published works were interpreted or reinterpreted by this review:

- $K_4NpO_2(CO_3)_{3(s)}$ and $(NH_4)_4NpO_2(CO_3)_{3(s)}$ solubility product were estimated from [66GOR/KLI] Gorbenko-Germanov and Klimov's and from [71MOS5] Moskvin's solubility measurements (despite the completely erroneous Moskvin's interpretation of his experimental results).
- Too few other solubility data are available [97VIT/CAP], nevertheless they were used to estimate the solubility product of $NpO_2CO_{3(s)}$ and the formation constants of the mononuclear intermediary complexes, $NpO_2(CO_3)_2^{2-}$ and $NpO_2CO_{3(aq)}$.
- As for Uranium [92GRE/FUG], Maya [84MAY] showed evidence of formation of at least one polynuclear mixed hydroxide-carbonate. Unfortunately in this potentiometric study the total concentration of Np(VI) was kept practically constant. This does not allow to interpret formation of polynuclear complexes (see the discussion on [84MAY] in the Appendix A). Maya proposed the formation of $(NpO_2)_2(OH)_3CO_3^-$ which seems quite reasonable when comparing with Uranium; but, for the reasons explained below and in the Appendix A, no accurate quantitative interpretation could be extracted from this work. Nevertheless, this review used those experimental data.

The other published works did not produce accurate data, or investigated too small concentration ranges of the key chemical species: most of them are consistent with the data (formation constants of the above carbonate complexes) selected by this review, eventually as reinterpreted by this review; but it was not possible to deduce quantitative information on minor species from them. Concerning the determination of the stoichiometry of Np(VI) soluble complexes, besides the

$$NpO_2(CO_3)_3^{-4} + e^- \Leftrightarrow NpO_2(CO_3)_3^{-5}$$

equilibrium first studied by Simakin, there are accurate published data only for the dissociation of the limiting complex into $(NpO_2)_3(CO_3)_6^{-6}$ [86GRE/FUG, 89RIG]. The corresponding uranium species are also stable [92GE/FUG] in similar

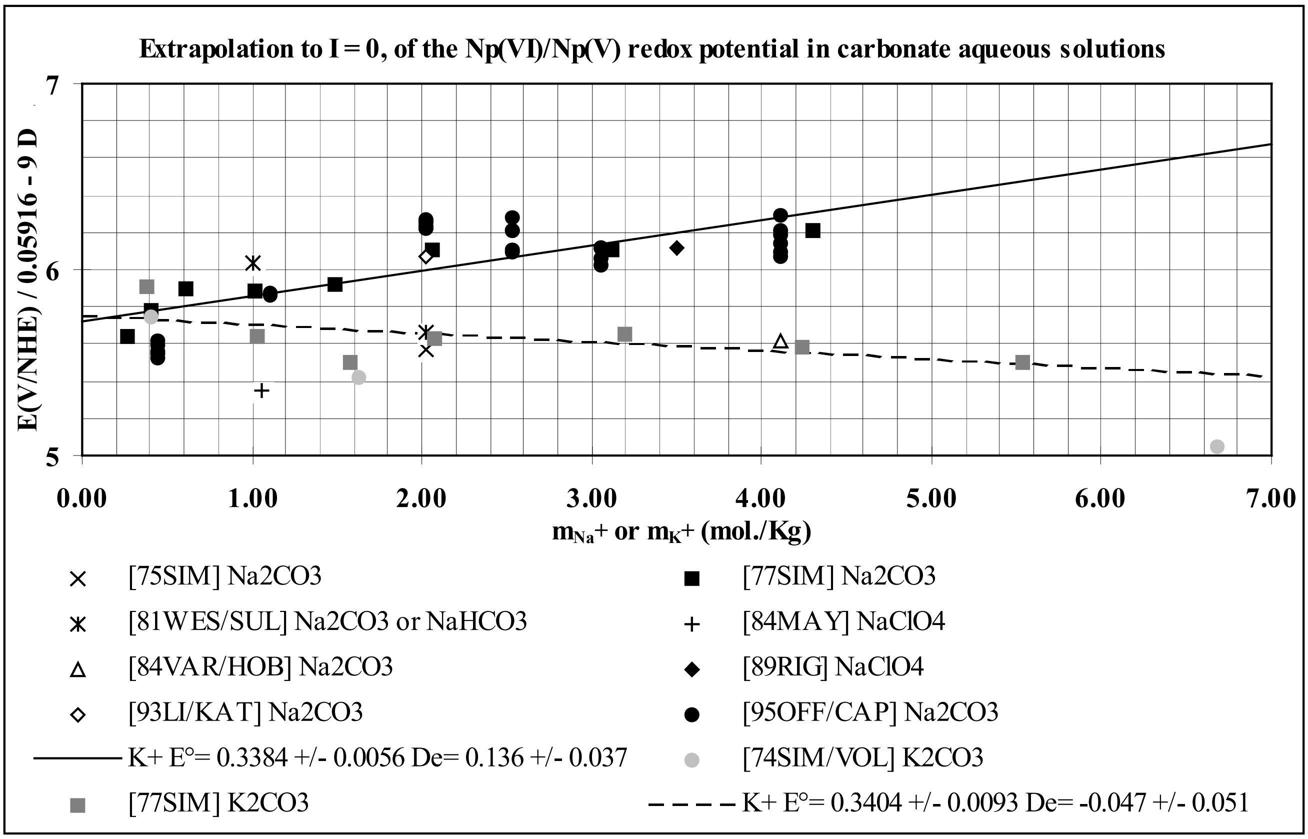


Figure VI-1: Extrapolation to zero ionic strength of the Np(VI)/Np(V) redox potential measured in Na^+ and K^+ carbonate media. The works from two different laboratories: Simakin [77SIM] and Vitorge [89RIG, 95OFF/CAP] were used for this extrapolation (black and dark grey points). The other ones were not reliable enough (see text) and where then not used to select standard value, among them [93LI/KAT] and one of [81WES/SUL] data are in agreement with the selection of this review. The (small) difference between Na^+ and K^+ media can clearly be interpreted as activity coefficient effect.

chemical conditions. There not enough correct published data to determine the stoichiometry of other Np(VI) species. This review usually used analogy with uranium to estimate their stability.

The carbonate complexes are formed in similar conditions as for Uranium. At high ionic strength (3 M $NaClO_4$) a regular progression among the U, Np, Pu series was observed for the formation and stepwise constants, and for $NpO_2CO_{3(s)}$ solubility product. The limiting and the trinuclear Np(VI) complexes are a little less stable than the corresponding Uranium ones, while the solubility products are probably of the same order of magnitude [97OFF/CAP] for Uranium and Neptunium, consequently Np(VI) solubility in carbonate-bicarbonate (3 M $NaClO_4$) media is lower for Np(VI) than for U(VI). The trinuclear Np(VI) complex is then only observed in (thermodynamically) over saturated conditions; but for kinetic reason (very much slower precipitation for Np(VI) than for U(VI) and Pu(VI)) it was probably present in several studies and it is the easiest trinuclear species to be studied among the U, Np, Pu series.

Beside these studies from which equilibrium constants and then Δ_rG_m were extracted, other thermodynamic parameters are proposed from Offerlé, Capdevila et al. study of the variation of redox potential with temperature [95OFF/CAP], and from Ullman and Schreiner calorimetric measurements [88ULL/SCH].

2.1.1.1. Np(VI) carbonate limiting complex

The starting point of this review, was the determination of the stoichiometry and the stability of the Np(VI) carbonate limiting complex. One of the first study of Np(VI) in carbonate media, was the preparation and characterisation of the $K_4NpO_2(CO_3)_{3(s)}$ solid [66GOR/KLI]. Its solubility was interpreted by this review (Appendix A) using analogy with Uranium, with the

$$K_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ K^+$$

equilibrium. The stoichiometry of the limiting complex, $NpO_2(CO_3)_3^{4-}$, was proposed only later by Simakin [77SIM]: careful measurements showed the potential of the Np(VI)/Np(V) redox couple is constant in concentrated sodium and potassium carbonate media of various concentrations, it was then concluded that the carbonate limiting complexes of Np(VI) and Np(V) have the same stoichiometry. In the same work $NpO_2(CO_3)_3^{5-}$ was proposed to be the Np(V) limiting complex from slope analysis of Np(V) solubility controlled by the

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 3\ Na^+$$

equilibrium. This two step demonstration implicitly assumed (at each step) that no polynuclear soluble complex was formed. Fortunately this is the case in these particular conditions as demonstrated later by Riglet for Np(V) [89RIG] and Grenthe, Riglet and Vitorge for Np(VI) [86GRE/FUG, 89RIG], using spectrophotometric measurements in both cases.

Due to lack of other reliable data, this review only used potential measurements of the

$$NpO_2(CO_3)_3^{-4} + e^- \Leftrightarrow NpO_2(CO_3)_3^{-5} \qquad \text{(VI.1)}$$

redox equilibrium.

Simakin reported junction potential measurements that were not so easy to understand. It also seemed that there was an inversion in the caption of the K^+ and Na^+ figure digitised by this review to get the original measurements (both in the English translation and in the original paper in Russian). Nevertheless, this review extracted normal potential versus the standard reference electrode.

Two different studies were published by Vitorge and co-workers. One was hidden in the Uranium paragraph of Riglet's thesis page 104 of the reference [89RIG]. Her experimental methodology was correct, and the experimental set up was also checked with Uranium in the same work, and indeed produced consistent results [92GRE/FUG]. In the other one Offerlé, Capdevila and Vitorge [95OFF/CAP] gave all the needed experimental details and original data. This review checked the treatment of the data: despite small errors pointed out by two of the authors, Capdevila and Vitorge, in this work and in a later report [97VIT/CAP] this review extracted a standard potential value that was consistent with the original Offerlé's one.

Statistical analysis was also performed independently on the two [77SIM, 95OFF/CAP] publications that reported enough data (table VI.a): uncertainty estimation was consistent with the estimations of the authors. Then this review performed extrapolation to zero ionic strength by using the SIT: the results of these three determinations appeared to be in very good agreement (figure VI.a). Small correction was also performed for the dissociation of the Np(V) limiting complex (see the discussion on references [77SIM, 95OFF/CAP] in the Appendix).

Other measurements (table VI.a, figure VI.a) of the potential of the same redox equilibrium were reported in the literature; but they did not include enough experimental information on reference electrode calibration, so this review systematically increased the uncertainty for possible junction potential contribution. This deviation was quite clear for Simakin, Volkov et al. [74SIM/VOL] and Simakin [75SIM] previous measurements. It was also probably present in Maya [84MAY] and Varlashkin, Hobart et al. [84VAR/HOB] measured values. In opposition one of Wester and Sullivan measurements [81WES/SUL], and Li, Kato et al. [93LI/KAT] measurement agree with the above [77SIM, 89RIG, 95OFF/CAP] values. Nevertheless, for the determination of the standard value, this review only used values of references [77SIM, 89RIG, 95OFF/CAP] giving evidence of correct calibration of reference electrode.

Since the potentials were converted to standard unit (ACTUALLY I DID NOT PERFORMED THE atm to bar CORRECTION which is 0.1 mV, much less than uncertainty), using the conventions adopted by this review (§ II.1.6.5 AS IN THE PREVIOUS VOLUME OF THIS SERIES [95SIL/BID]?) The above equilibrium is another notation for the

$$NpO_2(CO_3)_3^{-4} + H^+ \Leftrightarrow NpO_2(CO_3)_3^{-5} + \frac{1}{2} H_{2(g)} \qquad (VI.1)$$

equilibrium (where H^+ and $H_{2(g)}$ are in standard conditions) and the standard potential value was calculated by this review using unweighted SIT linear regression on experimental data in Na^+ media from references [77SIM, 89RIG, 95OFF/CAP]

$$E°(VI.1, 298.15\ K) = (0.338_4 \pm 0.005_6)\ V/SHE$$

then $$\Delta_rG°_m(VI.1, 298.15\ K) = -(32.6_5 \pm 0.5_4)\ kJ.mol^{-1}$$

This SIT regression also produced $\Delta\varepsilon = 0.13_6 \pm 0.0.3_7$ kg.mol.$^{-1}$, then $\varepsilon(Na^+,NpO_2(CO_3)_3^{-4}) = -0.49 \pm 0.21$ kg.mol.$^{-1}$ is calculated and selected by this review, using the $\varepsilon(Na^+,NpO_2(CO_3)_3^{-5}) = -0.63 \pm 0.21$ kg.mol.$^{-1}$ value selected by this review. This E°(VI.1, 298.15 K) value was combined with the $NpO_2(CO_3)_3^{-5}$ formation constant selected by this review ($\log_{10}\beta_3^V = 5.48 \pm 0.24$) to propose the $NpO_2(CO_3)_3^{-4}$ formation constant, β_3

$$\log_{10}\beta_3(VI.2, 298.15\ K) = 19.35 \pm 0.27$$

then $$\log_{10}\Delta_rG°_m(VI.2, 298.15\ K) = (-110._{46} \pm 1._{52})\ kJ.mol^{-1}$$

corresponding to the following equilibrium:

$$NpO_2^{+2} + 3\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_3^{-4} \qquad (VI.2)$$

2.1.1.2. Carbonate mononuclear Np(VI) complexes

Beside the above limiting complex $NpO_2(CO_3)_3^{-4}$, there are not any reliable published work proposing correct formation constant of the other mononuclear carbonate complex. They are the intermediary product of the limiting complex dissociation (to NpO_2^{+2}) at low Np(VI) total concentration (to avoid the formation of polynuclear complexes).

Maya [84MAY] interpreted his potentiometric titration with the $NpO_2(CO_3)_2^{-2}$ species; but this review found that the original experimental data were possibly not reliable (due to oversaturation) and that the interpretation proposed by Maya excluded $NpO_2CO_{3(aq)}$ and $(NpO_2)_3(CO_3)_6^{-6}$ that should certainly not be neglected in some of the measurements. A better interpretation could not be proposed by this review for kinetic reasons and for lack of experimental data in certain chemical conditions: high carbonic gas partial pressure and varying the total Np(VI) concentration (Appendix A). This review did not considered Maya's values for the $NpO_2(CO_3)_2^{-2}$ formation constants; but it is in reasonable agreement with the one selected by this review (Table VI.a) as expected, because $NpO_2(CO_3)_2^{-2}$ complex was one of the major dissociation product of the limiting complex at the begining of several titrations where Np(VI) was not or not too much oversaturated. In the same publication [84MAY], Maya reported the variation of the Np(VI)/Np(V) redox potential with chemical conditions. The formation constants he extracted from this electrochemical work were not much consistent with the interpretation of his potentiometric titration. He did not give very clear and convincing reason for this discrepancy. This review reinterpreted Maya's electrochemical measurement (Appendix A°), and found that the observed variations were mainly due to the dissociation of the Np(V) limiting complex, which was known independently (and then without curve fitting). Still dissociation constants of the Np(VI) could be obtained by this review as curve fitting results; but (table VI.a) with big uncertainty.

Moskvin [75MOS] recently followed by Pratopo, Moriyama et al. [93PRA/MOR, 95MOR/PRA] reported formation constant values; but their interpretation are completely in error, and reinterpretation (when feasible) can give information only on the limiting complex since it was the only major soluble complex present all over their solubility measurements despite what they said (see the discussion on their work and on [97VIT/CAP] in Appendix A).

Finally this review accepted the $NpO_2CO_{3(aq)}$ and $NpO_2(CO_3)_2^{-2}$ formation constants recently proposed by Vitorge

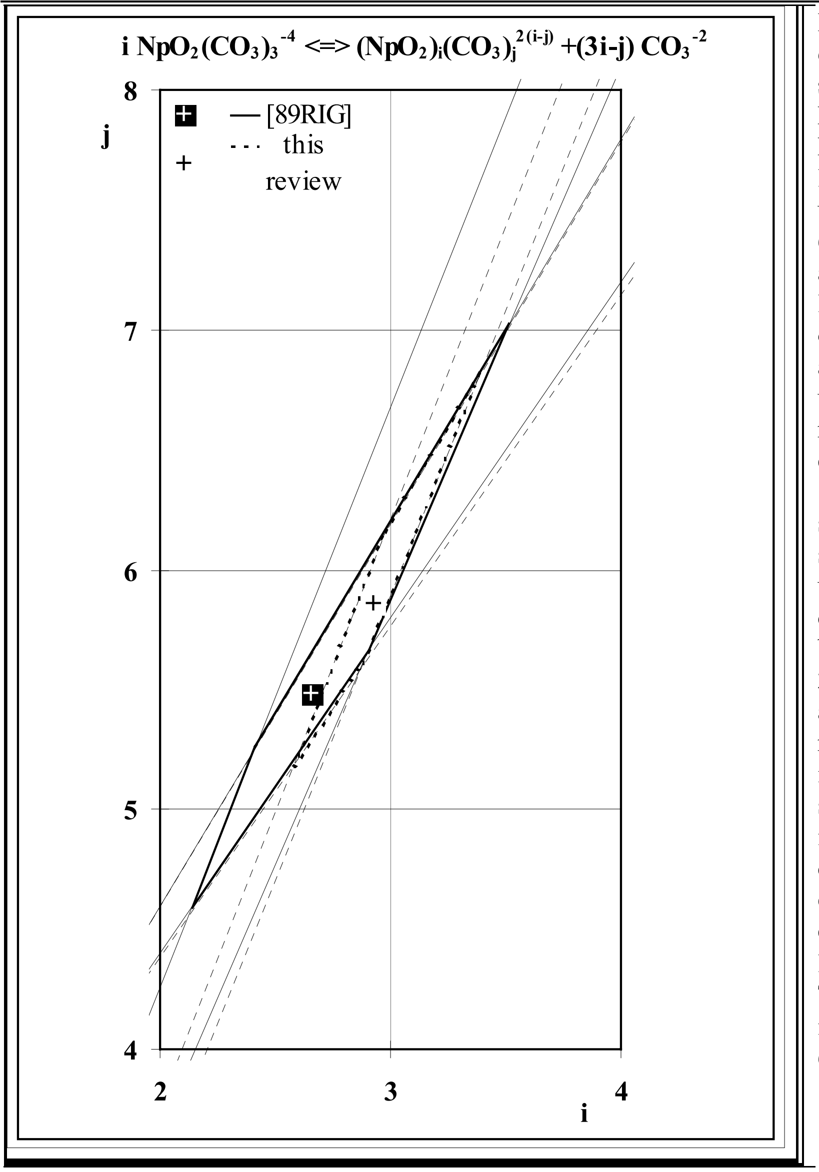


Figure VI-2: Result of the graphical determination of the stoichiometry of the soluble complex in equilibrium with the Np(VI) limiting complex in 1 to 10 mM Np(VI) aqueous bicarbonate solutions: the limiting complex is $NpO_2(CO_3)_3^{-4}$. The unknown dissociated complex is $(NpO_2)_i(CO_3)_j^{2(i-j)}$. Absorbance measurements at 670 and 700 nm were plotted versus $\log_{10}[CO_3)^{-2}]$ for each $[Np(VI)]_{total}$. The slope of this type of curves at the half reaction point, and their shift versus $\log_{10}[Np(VI)]_{total}$ were used to calculate two (theoretical linear) relationships involving the stoichiometric coefficients, i and j (see Appendix A and [89RIG]). The corresponding 2 lines (not shown on the figure) intercept at the resulting stoichiometry (crosses on the figure). The uncertainty on the graphical slope determinations are represented by the domain between two parallel lines (there are then 2 x 2 = 4 lines for the author determination, and also 4 (dashed) lines for this review reinterpretation (at 670 nm). The limit of the intersection of the domain is bolded: stoichiometric coefficients can only be i and j integer values falling inside this bolded domain. The original determination [89RIG] estimated graphically the slopes and corresponding uncertainties. This review used linear regressions and corresponding 1.96 σ. The result of both determinations is the same: i = 3, j = 6, the dissociated complex is then $(NpO_2)_3(CO_3)_6^{-6}$.

and Capdevila [97VIT/CAP] in 3 M $NaClO_4$ media (Table VI.a), despite there were determined from too few $NpO_2CO_{3(s)}$ solubility measurements as pointed out by the authors. Extrapolation to zero ionic strength

$$\log_{10}\beta°_2(\text{VI.3, 298.15 K})) = 16.4_7 \pm 0.5_8$$

$$\log_{10}\beta°_1(\text{VI.4, 298.15 K})) = 9.1_0 \pm 0.9_9$$

then $$\log_{10}\Delta_rG°_m(\text{VI.3, 298.15 K}) = (-93._{99} \pm 3._{30})\ \text{kJ.mol}^{-1}$$

$$\log_{10}\Delta_rG°_m(\text{VI.4, 298.15 K}) = (-51._{96} \pm 5._{66})\ \text{kJ.mol}^{-1}$$

corresponding to the $$NpO_2^{+2} + 2\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_2^{-2} \qquad (VI.3)$$

$$NpO_2^{+2} + CO_3^{-2} \Leftrightarrow NpO_2CO_3 \qquad (VI.4)$$

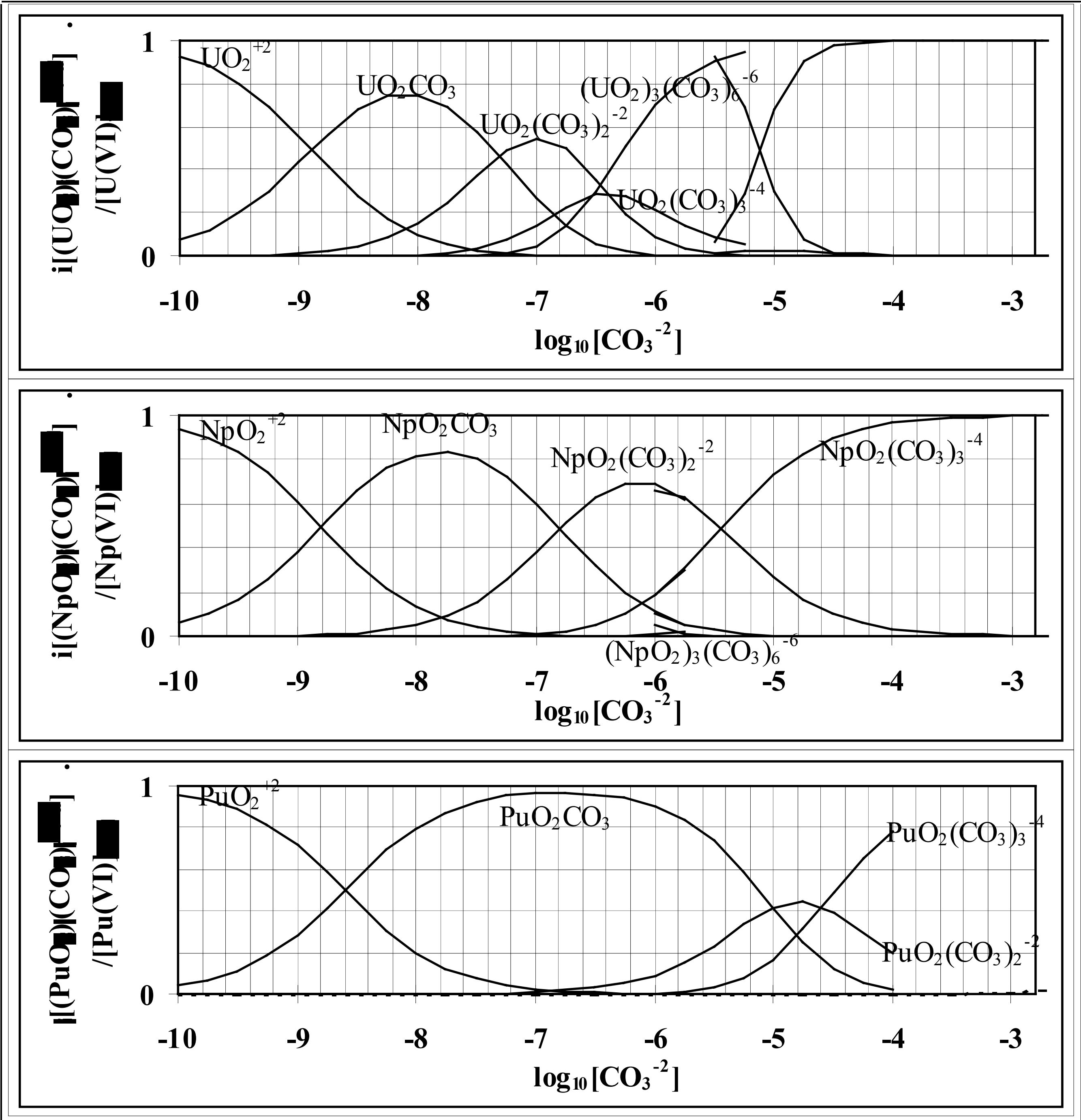
equilibria, used the following estimation of the specific interaction coefficients: 0 for $NpO_2CO_{3(aq)}$ as for all the uncharged species (Appendix B) and the same as the corresponding Uranium one for $NpO_2(CO_3)_2^{-2}$, $\varepsilon(Na^+,UO_2(CO_3)_2^{-2})$ =-0.02 kg.mol.$^{-1}$ [92GRE/FUG, 95SIL/BID].

2.1.1.3. The carbonate trinuclear Np(VI) complex

The trinuclear complex $(MO_2)_3(CO_3)_6^{-6}$, was first identified for Uranium (hence M = U) by Grenthe and searchers from his laboratory in 1981: see the [92GRE/FUG] review. A few years later, during a sabbatical leave in Vitorge's laboratory he used spectrophotometric technique to demonstrate that Neptunium and Plutonium also form the corresponding trinuclear complex [86GRE/RIG]. Concerning Neptunium, it was a part of Riglet's thesis [89RIG]. Stoichiometry determination, sensitivity analysis, uncertainty estimation and quantitative interpretation (i.e. determination of the equilibrium constant value) had been performed graphically. So this review used the original data tabulated in reference [89RIG] to interpret them with standard curve fitting programs: the same results with increased uncertainty (following the rules adopted by this review to estimate uncertainty) were found (tableVI.a) for the

$$3\ NpO_2(CO_3)_3^{-4} \Leftrightarrow 3\ CO_3^{-2} + (NpO_2)_3(CO_3)_6^{-6} \qquad (VI.5)$$

equilibrium. The trinuclear Neptunium complex is less stable than the Uranium one, while the carbonate solid compounds of these two actinide(VI) are of very similar stability. For this reason it is more difficult to obtain the Np(VI) trinuclear complex in equilibrium conditions than the corresponding Uranium one; but it was nevertheless observed practically pure in over saturated solutions. This was used to check the stoichiometry of this complex with a combination of classical and original graphical slope analysis (figure VI.b).



Figures VI-3: Np(VI) speciation in bicarbonate/carbonate aqueous solutions equilibrated with $AnO_2CO_{3(s)}$ or $Na_4UO_2(CO_3)_{3(s)}$ solid phase. Discontinuity of the calculated curves corresponds to the transformation of the solid phase (into the other one). Quite regular shift of the equilibrium constant and the corresponding stability domains, are observed along the partial actinide series U, Np and Pu. The trinuclear Plutonium species is the most difficult species to detect among the U, Np and Pu series; but it was nevertheless observed as for Np(VI). Pu data were taken from reference [87ROB/VIT] that certainly overestimates $PuO_2CO_{3(aq)}$ stability.

For the above reason and because there is anyhow much less published information on neptunium than on Uranium, it was very difficult to find other published data showing evidence of the $(NpO_2)_3(CO_3)_6^{-6}$ complex and of good enough quality to determine its formation constant at different ionic strength. Only the Maya's potentiometric titration [84MAY] at the highest P_{CO_2} (= $10^{-1.52}$ atm) was finally used to estimate $\log_{10}(\beta_{3,6}/(\beta_3))$(VI.5, 298.15 K, 1 M $NaClO_4$)) = $-8.8_1 \pm 1.0_7$ despite the kinetic and methodological problems already mentioned above, and the difficulty to evaluate the influence of $NpO_2(CO_3)_2^{-2}$ and $(NpO_2)_2(OH)_3CO_3^-$ formations (Appendix A) as reflected in uncertainty.

There were then only two data for extrapolation to zero ionic strength (which is not really enough for SIT linear regression). Analogy with Uranium should not be used because complexes with very negative charge (-5 and -6) often have unusual ε coefficients, probably due to ion pairing, and this was effectively found for Uranium trinuclear complex $(UO_2)_3(CO_3)_6^{-6}$. So rather than no standard value at all, this review preferred to extract

$$\log_{10}(\beta°_{6,3}/\beta°_3{}^3)(\text{VI.5, 298.15 K}) = -8._{27} \pm 2._{35}$$

(where uncertainty has been increased from 0.82 to 2.35) from the only two available data: at I = 1 M [84MAY] as reinterpreted by this review, and 3 M [86GRE/ROB, 89RIG].

then $$\log_{10}\Delta_rG°_m(\text{VI.5, 298.15 K}) = (47._{22} \pm 13._{42})\ \text{kJ.mol}^{-1}$$

This also produced Δε(VI.5, 298.15 K) = 0.49 ± 0.49 $mol.kg^{-1}$; then $\varepsilon((NpO_2)_3(CO_3)_6^{-6},Na^+) = -0.7_5 \pm 0.8_1\ mol.kg^{-1}$. This values is different from the corresponding Uranium one (0.37 ± 0.11 $mol.kg^{-1}$) [92GRE/FUG, 95SIL/BID]; but as already pointed out [92GRE/FUG] the Uranium value is itself quite unusual: negative ε values are usually observed for negatively charged complexes.

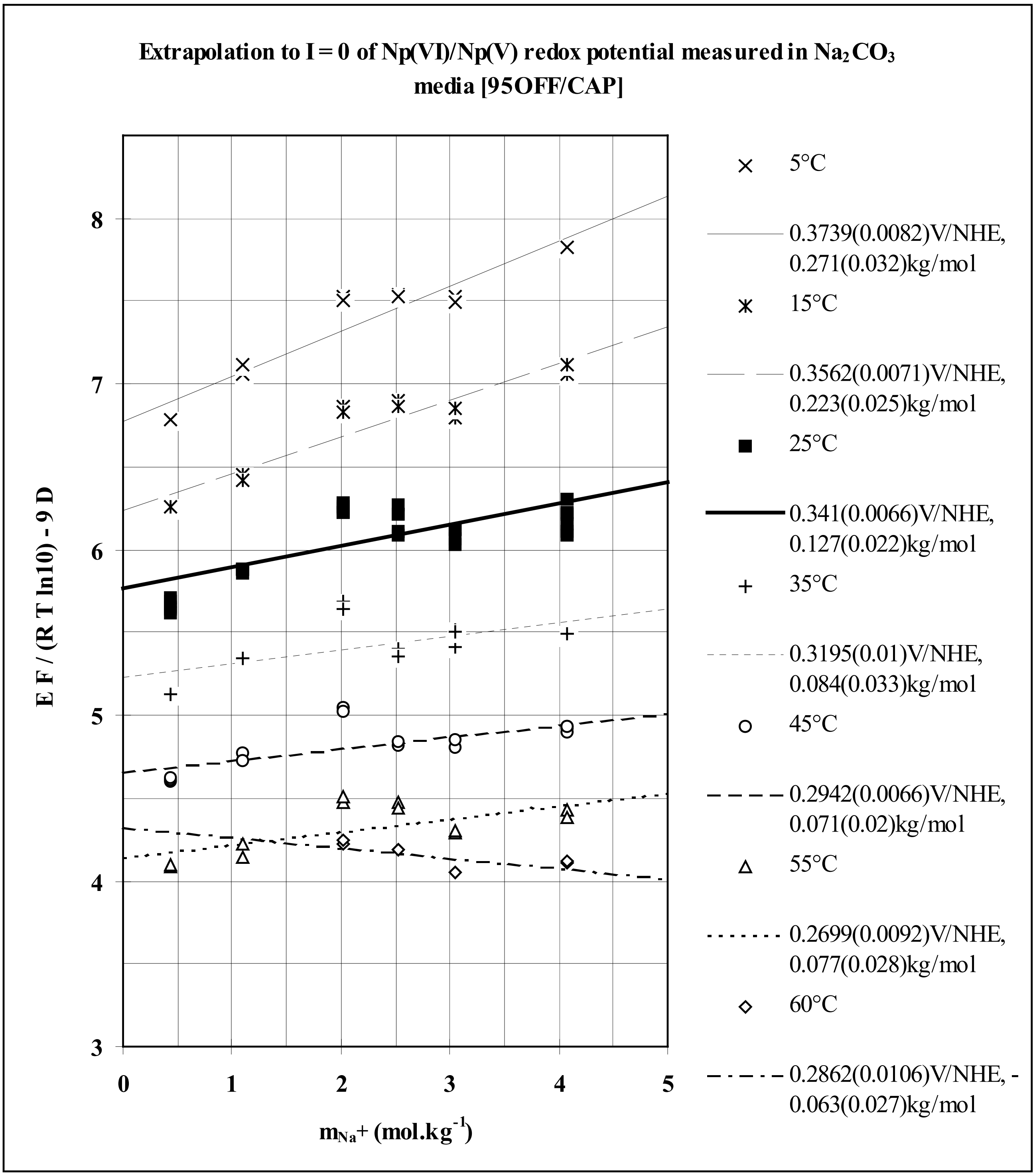


Figure VI-4: Extrapolation to zero ionic strength of the Np(VI)/Np(V) redox potential at different temperatures. The E(T,0) and Δε(T) written on the figure, are the results of SIT linear regressions performed at each temperature from the E(T,I) data measured by Offerlé [95OFF/CAP]. NHE should be written SHE.

Combining the above $\log_{10}(\beta°_{6,3}/\beta°_3{}^3)$ and $\log_{10}\beta°_3$ values, one deduces the $(NpO_2)_3(CO_3)_6{}^{-6}$ formation constant

and $\log_{10}\beta°_{6,3}(VI.6, 298.15\ K)) = 49._{78} \pm 2._{48}$

then $\log_{10}\Delta_rG°_m(VI.6, 298.15\ K) = (-284._{15} \pm 14_{.18})\ kJ.mol^{-1}$

for equilibrium $3\ NpO_2{}^{+2} + 6\ CO_3{}^{-2} \Leftrightarrow (NpO_2)_3(CO_3)_6{}^{-6}$ (VI.6)

2.1.1.4. Mixed hydroxide-carbonate complexes of Np(VI)

There is evidence of mixed (hydroxide-carbonate) complex from Maya's publication [84MAY]; but as already discussed above and in Appendix A, this work did not vary the total Np(VI) concentration which does not allow to determine polynuclear complex stoichiometry, and the solution was probably oversaturated. So this review considered some of the proposed constant values (or some finally rejected by Maya, or recalculated by this review from Maya's data) as

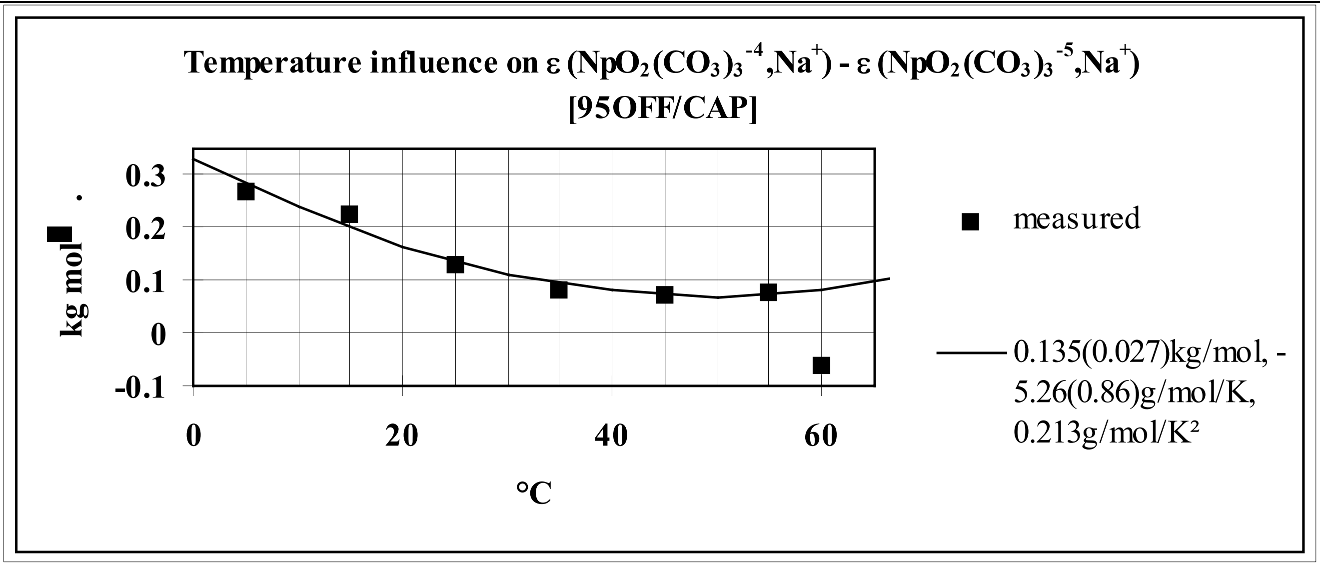


Figure VI-5: Temperature influence on the specific intertaction coefficient change for the Np(VI)/Np(V) redox equilibrium in Na_2CO_3 media. The line is plotted with a second order polynomial regression. The fitted values of its zero, first and second order terms were used to obtain Δε(T°), Δε'(T°) and Δε"(T°) respectively written on the figure. The points were measured Δε(T) by Offerlé [95OFF/CAP].

possible maximum values (table VI.a), and still accept the $(NpO_2)_2(OH)_3CO_3^-$ one: $\log_{10}({}^*\beta_{2,1,3}/(\beta_3{}^2)$(VI.7, 298.15 K, 1 M $NaClO_4$)) = $-21.1_6 \pm 1.6_7$ for

$$2\ NpO_2(CO_3)_3^{-4} + 3\ H_2O \Leftrightarrow 3\ H^+ + 5\ CO_3^{-2} + (NpO_2)_2(OH)_3CO_3^- \qquad (VI.7)$$

equilibrium; but no standard value is proposed. Similar work on Uranium by the same author, was found to overestimate formation constants of mixed uranium complexes as selected by the [92GRE/FUG] review. As a guide line, values selected for U(VI) in [92GRE/FUG] could also be used.

2.1.1.5. Temperature influence on the stability of the limiting carbonate complex of Np(VI)

Offerlé Capdevila and Vitorge also studied the Np(VI)/Np(V) redox equilibrium at different temperatures (and ionic strengths). The data are in the table VIc together with their extrapolation to zero ionic strength at different temperatures. The data and the interpretation were checked by this review as explained above for the data at 25°C (Appendix A). Local approximation using classical thermodynamic differential equations were used to derived Δ_rS_m, Δ_rH_m and Δ_rCp_m, at 25°C, the data previously extrapolated to zero ionic strength gave the corresponding standard values. This review checked (Appendix A) the consistency of the local temperature approximation by testing three different ways to treat the data with the same qualitative initial approximation: Δ_rCp_m has small influence in the temperature range studied. Numerical results were consistent with this assumption and the three treatments of the data agreed. It was also checked that the combination of ionic strength and temperature corrections gave the same results whatever the order to perform them. Finally the results found by this review were consistent with those initially calculated by Offerlé, Capdevila and Vitorge (table VI.d).

$$\Delta_rH°_m(\text{VI.1, 298.15 K}) = (-88._{77} \pm 2._{93})\ \text{kJ.mol}^{-1}$$
$$\Delta_rS°_m(\text{VI.1, 298.15 K}) = (-187._6 \pm 9._7)\ \text{kJ.mol}^{-1}$$
$$\Delta_rCp°_m(\text{VI.1, 298.15 K}) = (-759 \pm 141)\ \text{kJ.mol}^{-1}$$

As pointed out by Offerlé, Capdevila and Vitorge [95OFF/CAP], similar $\Delta_rS°_m$ and $\Delta_rCp°_m$ values were found in the same laboratory for the corresponding Uranium and Plutonium equilibria using the same methodology, and they are consistent with data selected by Grenthe, Fuger et al. [92GRE/FUG].

In the same way, temperature influence on Δε was studied. (table VI.c, figure VI-5 and Appendix A).

Δ_rH_m(VI.2, 298.15 K) was measured by Schreiner, Friedman at al. [85SCH/FRI] and by Ullman and Schreiner [88ULL/SCH]. As for their corresponding Uranium measurement [92GRE/FUG] sulphate complexation should be subtracted from one of their measurements that are then consistent and accepted by this review (Appendix A). It also needs to be corrected to zero ionic strength. These corrections were claimed to be negligible for Uranium [92GE/FUG]. This review estimated the ionic strength influence from the data at the end of the titration where the limiting complex was already formed and only the ionic strength was varying (Appendix A) and found it to be indeed negligible. Anyhow uncertainty was increase to the same value as for Uranium [92GRE/FUG]

$$\Delta_rH°_m(\text{VI.2, 298.15 K}) = (-42.0 \pm 4.1)\ \text{kJ.mol}^{-1}$$

2.1.1.6. Discussion

The Np(VI) carbonate complex (and compound: see below) data selected in this review are quite similar to the corresponding Uranium and Plutonium ones. Small regular variation is usually observed among the partial U, Np, Pu series; but this can have practical effect as discuss above for the stability of the carbonate trinuclear complexes; and as illustrated in the figure VI.3.

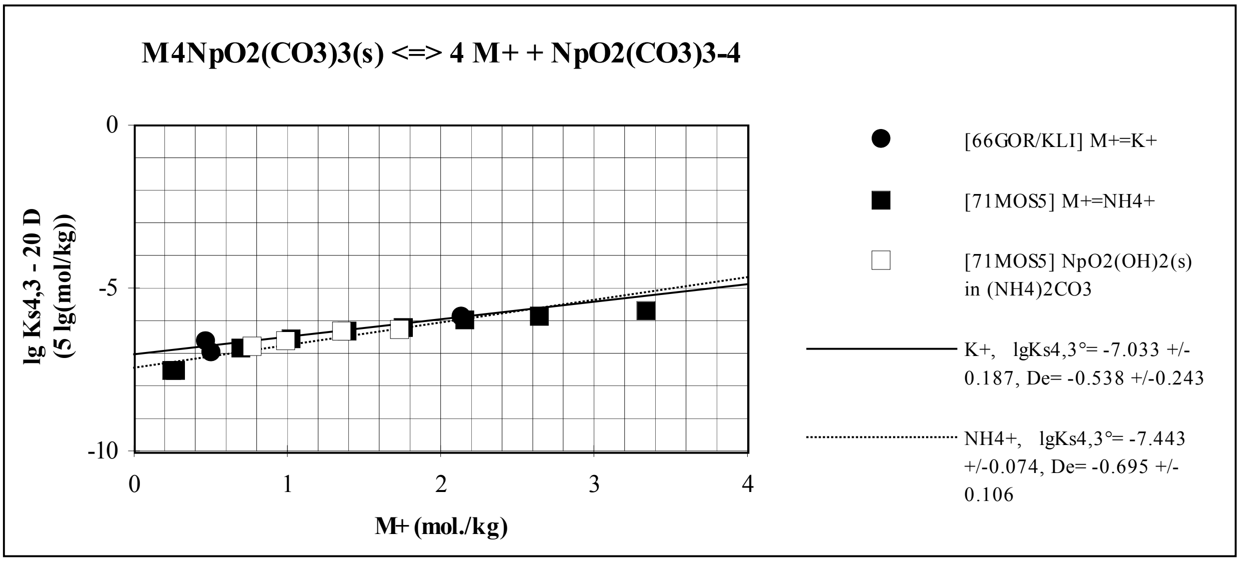


Figure VI-6: Extrapolation to I=0 of the $M_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ M^+$ equilibrium constant, Ks_3 using the SIT (appendix B). $\log_{10}Ks_3$ - 20 D is plotted as a function of M^+ molality ($M^+ = K^+$ or NH_4^+). The data are taken from the references indicated on the figure as interpreted [66GOR/KLI] or reinterpreted [71MOS5] by this review (appendix A). They refer to aqueous M_2CO_3 media. The results of linear regressions (lines) are indicated on the figure. Uncertainty on each experimetal point is 0.4

2.2. Neptunium(VI)-carbonate compounds

This review

- interpreted Gorbeko-Germanov and Klimov [66GOR/KLI] solubility measurements,
- reinterpreted Moskvin's ones [71MOS5]

with respectively the following equilibria

$$(NH_4)_4NpO_2(CO_3)_{3(cr)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ (NH_4)^+ \qquad (VI.8)$$

$$K_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ K^+ \qquad (VI.9)$$

but no data could be estimated for

$$Na_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ Na^+ \qquad (VI.10)$$

Despite the solid phase was not characterised. The corresponding equilibrium constants (Table VI.a) were extrapolated to zero ionic by performing linear SIT regression (calculations are in the Appendix A). The $\Delta\varepsilon$ values for the reaction (VI.8) and (VI.9) were respectively -0.70 ± 0.14 and -0.54 ± 0.37 from which were derived

$$\varepsilon(NpO_2(CO_3)_3^{4-},NH_4^+) = -0.78 \pm 0.37$$

$$\varepsilon(NpO_2(CO_3)_3^{4-},K^+) = -0.62 \pm 0.37$$

The standard equilibrium constant are

$$\log_{10}Ks_3(VI.8, 298.15\ K) = -7.44 \pm 1.11$$

$$\log_{10}Ks_3(VI.9, 298.15\ K) = -7.03 \pm 1.3$$

Vitorge and Capdevila's estimation of $NpO_2CO_{3(s)}$ solubility product [97CAP/VIT] was accepted and corrected to zero ionic strength:

$$NpO_2CO_{3(s)} \Leftrightarrow NpO_2^{+2} + CO_3^{-2} \qquad (VI.11)$$

$$\log_{10}Ks_0(VI.11, 298.15\ K) = -13.9_8 \pm 0.3_8$$

NOTE

THE $U(VI)_2M(VI)(CO_3)_6^{-6}$ were already selected in the Uranium review, I have re-examined the data (Appendix A) I suggest to keep the conclusion of the U review (that accepted the values of references [86GRE/RIG, 89RIG]), and then to reproduce what is in [92GRE/FUG and 95SIL/BID].

Tables

Table VI.a: Experimental equilibrium constants for the dioxoneptunium(VI)-carbonate-water system. Other species were proposed in the literature (two following tables). Standard values proposed by this review are bolded. When no reference is indicated, the corresponding value was calculated from data selected by this review.

medium	t(°C)	method	$\log_{10}K$	reference
β_3 $NpO_2^{+2} + 3\ CO_3^{-2} \Leftrightarrow \mathbf{NpO_2(CO_3)_3^{-4}}$				
I = 0	25	red,rev	$\mathbf{19.35_1 \pm 0.26_7}$	[77SIM, 89RIG, 95OFF/CAP]^{b}
I→0, $\Delta\varepsilon$=-0.05±0.08 in 2.09→0.13 M Na_2CO_3		red	19.33 ± 0.27	[77SIM]^{bf}
I→0, $\Delta\varepsilon$=0.13_5±0.03 in 2→0.22 M Na_2CO_3	25	vlt	19.36 ± 0.28	[95OFF/CAP]^{bj}
1 M $NaClO_4$, $10^{-5.5} \leq P_{CO_2} \leq$ 1atm, 2μM? Np(VI)	25	red	21.6	[84MAY]
1 M $NaClO_4$, $10^{-5.5} \leq P_{CO_2} \leq$ 1atm, 2μM? Np(VI)	25	red	≥19.2 ± 4.4	[84MAY]^{f}
1 M Na^+ or H^+, 0.11 M CO_3^{-2}, ClO_4^-, P_{CO_2}=1atm,	25	red	20.6 ± 1.5	[84MAY]^{f}
1 M $NaClO_4$, $10^{-3.5} \leq P_{CO_2} \leq$ 0.028atm, ≈1mM Np(VI)	25	pot	21.15± 0.12	[84MAY]
1 M Na^+, ClO_4^-	25	red,rev	20.17± 0.37	
3 M Na^+, ClO_4^-	25	red,sol	21.8 ± 0.4	[89RIG]^{f}
3 M Na^+, ClO_4^-	25	red,rev	22.05± 0.88	
β_2/β_3 $NpO_2(CO_3)_3^{-4} \Leftrightarrow NpO_2(CO_3)_2^{-2} + CO_3^{-2}$				
I = 0	25	rev	-3.0 ± 0.7	
1 M $NaClO_4$, P_{CO_2} $10^{-5.5}$ atm, 2μM? Np(VI)	25	red	-4.51	[84MAY]
1 M $NaClO_4$, P_{CO_2} $10^{-5.5}$ atm, 2μM? Np(VI)	25	red	≤-5.72 ± 1.96	[84MAY]^{f}
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq$ 0.028atm, ≈1mM Np(VI)	25	pot	-4.64 ± 0.18	[84MAY]
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq$ 0.028atm, ≈1mM Np(VI)	25	pot	$-4.7_4 \pm 0.7$	[84MAY]^{f}
1 M $NaClO_4$	25	rev	$-4.9_7 \pm 0.7$	
3 M $NaClO_4$, P_{CO_2} 1 atm	22±1	sol,rev	$-6.3_3 \pm 0.7$	[97VIT/CAP]^{b}
β_2 $NpO_2^{+2} + 2\ CO_3^{-2} \Leftrightarrow \mathbf{NpO_2(CO_3)_2^{-2}}$				
I = 0	22±1	sol	$\mathbf{16.4_7 \pm 0.5_8}$	[97VIT/CAP]^{bk}
1 M $NaClO_4$, P_{CO_2} $10^{-5.5}$ atm, 2μM? Np(VI)	25	red	13.5 ± 4.8	[84MAY]
1 M $NaClO_4$, P_{CO_2} $10^{-5.5}$ atm, 2μM? Np(VI)	25	red	≤14.9 ± 2.1	[84MAY]^{f}
1 M $NaClO_4$, $10^{-3.5} \leq P_{CO_2} \leq$ 0.028atm, ≈1mM Np(VI)	25	pot	16.51± 0.14	[84MAY]
1 M $NaClO_4$, $10^{-3.5} \leq P_{CO_2} \leq$ 0.028atm, ≈1mM Np(VI)	25	pot	$15.4_3 \pm 0.5_5$	[84MAY]^{f}
1 M $NaClO_4$	25	rev	$15.20 \pm 0.5_4$	
3 M $NaClO_4$ P_{CO_2} = 1 atm	22±1	sol	$15.7_2 \pm 0.5_1$	[97VIT/CAP]^{j}
β_1/β_3 $NpO_2(CO_3)_3^{-4} \Leftrightarrow NpO_2CO_{3(aq)} + 2\ CO_3^{-2}$				
I = 0	22±1	rev	$-10._{25} \pm 1._{04}$	
1 M $NaClO_4$, P_{CO_2} $10^{-5.5}$ atm, 2μM? Np(VI)	25	red	≤-11.1±2.0	[84MAY]^{f}
1 M $NaClO_4$	25	rev	$-12.2_9 \pm 0.7$	
3 M $NaClO_4$, P_{CO_2} 1 atm	22±1	sol,rev	$-13.5_5 \pm 0.7$	[97VIT/CAP]^{b}
β_1 $NpO_2^{+2} + CO_3^{-2} \Leftrightarrow \mathbf{NpO_2CO_{3(aq)}}$				
I = 0	22±1	sol	$\mathbf{9.1_0 \pm 0.9_9}$	[97VIT/CAP]^{b}
1 M $NaClO_4$, P_{CO_2} $10^{-5.5}$ atm, 2μM? Np(VI)	25	red	≤9.5 ± 2.1	[84MAY]^{f}
1 M $NaClO_4$	25	rev	$7.8_8 \pm 0.9_8$	
3 M $NaClO_4$ P_{CO_2} = 1 atm	22±1	sol	$8.5_0 \pm 0.9_7$	[97VIT/CAP]^{j}
$^*\beta_{3,6}/\beta_3^3$ $3NpO_2(CO_3)_3^{-4}+6H^+ \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6}+3CO_{2(g)}+3H_2O$				
I = 0 from data in 3 and 1 M $NaClO_4$	25	rev	$46.1_8 \pm 2.3_5$	[86GRE/RIG, 84MAY^{g}]^{b}
1 M $NaClO_4$, $10^{-3.5} \leq P_{CO_2} \leq$ 0.028atm, ≈1mM Np(VI)	25	pot	$42._{45} \pm 2.9_0$	[84MAY]^{g}
1 M $NaClO_4$, P_{CO_2}=0.028atm, ≈1mM Np(VI)	25	pot	$42._{82} \pm 1.0_6$	[84MAY]^{f}
3 M $NaClO_4$, P_{CO_2}=0.1 to 1atm, 0.95 to 18.65mM Np(VI)	22±1	sp	42.8 ± 0.1	[86GRE/RIG, 89RIG]
3 M $NaClO_4$, P_{CO_2}=0.1 to 1atm, 0.95 to 18.65mM Np(VI)	22±1	sp	$42.7_9{}^{f} \pm 0.19$	[86GRE/RIG, 89RIG]

Table VI.a continued medium	t(°C)	method	$\log_{10}K$	reference
$\beta_{3,6}/\beta_3^3$ $3\ NpO_2(CO_3)_3^{-4} \Leftrightarrow 3\ CO_3^{-2} + \mathbf{(NpO_2)_3(CO_3)_6^{-6}}$				
I = 0, 3 and 1 M $NaClO_4$, **$\Delta\varepsilon = 0.49 \pm 0.49$** in Na^+ media then **$\varepsilon(Na^+,(NpO_2)_3(CO_3)_6^{-6}) = -0.75 \pm 0.81$**	25	rev	**$-8.2_7 \pm 2.3_5$**	[86GRE/RIG, 84MAY^g]^b
1 M $NaClO_4$, $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm, ≈1mM Np(VI)	25	pot	-9.2 ± 2.9	[84MAY]^g
1 M $NaClO_4$, P_{CO_2}=0.028atm, ≈1mM Np(VI)	25	pot	$-8.8_1 \pm 1.0_7$	[84MAY]^{fj}
3 M $NaClO_4$, P_{CO_2}=0.1 to 1atm, 0.95 to 18.65mM Np(VI)	22±1	sp	-10.0 ± 0.1	[86GRE/RIG, 89RIG]
3 M $NaClO_4$, P_{CO_2}=0.1 to 1atm, 0.95 to 18.65mM Np(VI)	22±1	sp	$-10.06^{fj} \pm 0.56$	[86GRE/RIG, 89RIG]
***$\beta_{2,1,3}/\beta_3$** $2NpO_2(CO_3)_3^{-4} + 7H^+ \Leftrightarrow 5CO_{2(g)} + 2H_2O + (NpO_2)_2CO_3(OH)_3^-$				
1 M $NaClO_4$, P_{CO_2}=0.028atm, ≈1mM Np(VI)	25	pot	41.76 ± 0.32	[84MAY]
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm, ≈1mM Np(VI)	25	pot	41.75 ± 1.46	[84MAY]^f
$\beta_{2,1,3}/\beta_3$ $2NpO_2(CO_3)_3^4 + 3H_2O \Leftrightarrow 5CO_3^{-2} + 3H^+ + \mathbf{(NpO_2)_2CO_3(OH)_3^-}$				
1 M $NaClO_4$, P_{CO_2}=0.028atm, ≈1mM Np(VI)	25	pot	-44.4 ± 0.3	[84MAY]
1 M $NaClO_4$, $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm, ≈1mM Np(VI)	25	pot	-44.4 ± 1.5	[84MAY]^f

Table VI.a continued medium	t(°C)	method	E(V/SHE)^{fij}	E(V/SHE)	reference
$E_{VI/V}$ $NpO_2(CO_3)_3^{-5} \Leftrightarrow \mathbf{NpO_2(CO_3)_3^{-4}} + e^-$					
I→0, $\Delta\varepsilon = 0.13_6 \pm 0.03_7$ in Na^+ media, then $\varepsilon(Na^+,NpO_2(CO_3)_3^{-4}) = -0.37 \pm 0.09$, $\Delta\varepsilon = -0.04_7 \pm 0.05_1$ in K^+ media	25	rev		**$0.338_4 \pm 0.005_6$**	[77SIM, 89RIG, 95OFF/CAP]^b
I→0, in 2.09→0.19 M Na_2CO_3 and K_2CO_3	?^{h}	rev		0.344 ± 0.013	[77SIM]^{bjf}
I→0, $\Delta\varepsilon=-0.08_1 \pm 0.02_5$ in 2.09→0.13 M Na_2CO_3	?^{h}	red		0.349 ± 0.003	[77SIM]^{bfj}
I→0, $\Delta\varepsilon=0.15 \pm 0.05$ in 2→0.22 M Na_2CO_3	25	vlt		0.341 ± 0.017	[95OFF/CAP]^j
I→0, $\Delta\varepsilon=0.12_1 \pm 0.04_3$ in 2→0.22 M Na_2CO_3	25	vlt		0.342 ± 0.013	[95OFF/CAP]^{bj}
I→0, $\Delta\varepsilon=0.04_7 \pm 0.05_1$ in 2.54→0.19 M K_2CO_3	?^{h}	red		0.340 ± 0.009	[77SIM]^{bfj}
0.13 M Na_2CO_3	?^{h}	red	0.421^{fij}	0.437 ± 0.010	[77SIM]^j
0.20 M Na_2CO_3	?^{h}	red	0.440^{fij}	0.447 ± 0.010	[77SIM]^j
0.22 M Na_2CO_3	25	vlt	0.428^{fij}	0.434 ± 0.004	[95OFF/CAP]^j
0.31 M Na_2CO_3	?^{h}	red	0.456^{fij}	0.459 ± 0.010	[77SIM]^j
0.51 M Na_2CO_3	?^{h}	red	0.466^{fij}	0.466 ± 0.010	[77SIM]^j
0.55 M Na_2CO_3	25	vlt	0.466^{fij}	0.467 ± 0.003	[95OFF/CAP]^j
0.74 M Na_2CO_3	?^{h}	red	0.475^{fij}	0.475 ± 0.043	[77SIM]^j
1 M Na_2CO_3, pH 11.5	25±0.3	red		0.46 ± 0.01^e	[75SIM]^{dj}
1 M Na_2CO_3 or 1 M $NaHCO_3$	?^{h}	red		0.465	[81WES/SUL]
1 M Na_2CO_3,	23±2	cou		0.49	[93LI/KAT]
1 M Na_2CO_3	25	vlt	0.500^{fij}	0.500 ± 0.003	[95OFF/CAP]^j
1.02 M Na_2CO_3	?^{h}	red	0.492^{fij}	0.492 ± 0.010	[77SIM]^j
1.25 M Na_2CO_3	25	vlt	0.500^{fij}	0.500 ± 0.009	[95OFF/CAP]^j
1.5 M Na_2CO_3	25	vlt	0.498^{fij}	0.498 ± 0.006	[95OFF/CAP]^j
1.53 M Na_2CO_3	?^{h}	red	0.499^{fij}	0.499 ± 0.010	[77SIM]^j
2 M Na_2CO_3	?^{h}	vlt		0.474	[84VAK/HOB]
2 M Na_2CO_3	25	vlt	0.507^{fij}	0.507 ± 0.010	[95OFF/CAP]^j
2.09 M Na_2CO_3	?^{h}	red	0.511^{fij}	0.511 ± 0.010	[77SIM]^j
1 (or 0.8) M $NaClO_4$, 0.2 M $NaHCO_3$	25	red		0.426 ± 0.087	[84MAY]
3 M $NaClO_4$	22±1	vlt	0.495^{fij}	0.496 ± 0.005	[89RIG]^j
0.19 M K_2CO_3	?^{h}	red		0.446 ± 0.010	[77SIM]^j
0.2 M K_2CO_3	20±1	red		0.43 ± 0.01^e	[74SIM/VOL]^d
0.51 M K_2CO_3	?^{h}	red		0.451 ± 0.010	[77SIM]^{fj}
0.78 M K_2CO_3	?^{h}	red		0.452 ± 0.010	[77SIM]^{fj}
0.8 M K_2CO_3	20±1	red		0.44 ± 0.01^e	[74SIM/VOL]^d
1.01 M K_2CO_3	?^{h}	red		0.464 ± 0.010	[77SIM]^{fj}
1.53 M K_2CO_3	?^{h}	red		0.473 ± 0.010	[77SIM]^{fj}

Table VI.a continued	medium	t(°C)	method	E(V/SHE)	reference
	1.99 M K_2CO_3	?[h]	red	0.473±0.010	[77SIM][fj]
	2.54 M K_2CO_3	?[h]	red	0.472±0.010	[77SIM][fj]
	3 M K_2CO_3	20±1	red	0.44 ±0.01[e]	[74SIM/VOL][d]

Table VI.a continued	medium	t(°C)	method	$log_{10}K$	reference
β_3^{VI}/β_3^{V}	$NpO_2(CO_3)_3^{-5} + NpO_2^{+2} \Leftrightarrow NpO_2^{+} + NpO_2(CO_3)_3^{-4}$				
	I = 0	25	rev	13.87 ± 0.12	
	1 M $NaClO_4$	25	red	12.06 ± 0.75	[84MAY][f]
	1 M $NaClO_4$	25	rev	11.48 ± 0.13	
	1 M Na_2CO_3,	23±2	cou	11.5	[93LI/KAT]
	3 M $NaClO_4$	22±1	vlt	11.3 ± 0.2	[89RIG][j]
	3 M $NaClO_4$	25	rev	11.13 ± 0.20	
	0.4 to 6 M K^+, 1 M ClO_4^-	20±1	red	11.2 ± 0.9	[74SIM/VOL][a]
K_s	**$NpO_2(CO_3)_{3(s)}$** $\Leftrightarrow NpO_2^{+2} + CO_3^{-2}$				
	I = 0	22±1	sol	**$-14.5_2 \pm 0.4_3$**	[97VIT/CAP][b]
	3 M $NaClO_4$ P_{CO_2} = 1 atm	22±1	sol	-13.98 ± 0.38	[97VIT/CAP][j]
$K_{s4}(K^+)$	**$K_4NpO_2(CO_3)_{3(s)}$** $\Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ K^+$				
	I→0 in 1→0.2 M K_2CO_3, $\Delta\varepsilon = -0.54\pm0.37$, then $\varepsilon(K^+,NpO_2(CO_3)_3^{4-}) = -0.62\pm0.42$	20±2	sol	**-7.03 ± 1.3**	[66GOR/KLI][ab]
	self dissolution	20±2	sol	-2.31 ± 0.4	[66GOR/KLI][a]
	0.2 M K_2CO_3 + self dissolution	20±2	sol	-2.81 ± 0.4	[66GOR/KLI][a]
	1 M K_2CO_3 + self dissolution	20±2	sol	-0.85 ± 0.4	[66GOR/KLI][a]
	5.573 M K_2CO_3 + self dissolution	20±2	sol	0.11 ± 0.4	[66GOR/KLI][a]
$K_{s4}(NH_4^+)$	**$(NH_4)_4NpO_2(CO_3)_{3(s)}$** $\Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ NH_4^+$				
	I→0 in 2.2→0.1 M $(NH_4)_2CO_3$, $\Delta\varepsilon=-0.70\pm0.14$ then $\varepsilon(NH_4^+,NpO_2(CO_3)_3^{4-}) = -0.78\pm0.37$	?[h]	sol	**-7.44 ± 1.11**	[71MOS5][bc]
	self dissolution	?[h]	sol	-3.42 ± 0.4	[71MOS5][c]
	0.1 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-3.48 ± 0.4	[71MOS5][c]
	0.5 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-2.33 ± 0.4	[71MOS5][c]
	0.75 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-1.82 ± 0.4	[71MOS5][c]
	0.75 M $(NH_4)_2CO_3$ + $NpO_2(OH)_{2(s)}$ dissolution	?[h]	sol	-1.90 ± 0.4	[71MOS5][c]
	1 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-1.43 ± 0.4	[71MOS5][c]
	1 M $(NH_4)_2CO_3$ + $NpO_2(OH)_{2(s)}$ dissolution	?[h]	sol	-1.45 ± 0.4	[71MOS5][c]
	1.25 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-1.20 ± 0.4	[71MOS5][c]
	1.25 M $(NH_4)_2CO_3$ + $NpO_2(OH)_{2(s)}$ dissolution	?[h]	sol	-1.25 ± 0.4	[71MOS5][c]
	1.5 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-0.90 ± 0.4	[71MOS5][c]
	1.8 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-0.66 ± 0.4	[71MOS5][c]
	2.2 M $(NH_4)_2CO_3$ + self dissolution	?[h]	sol	-0.47 ± 0.4	[71MOS5][c]

[a] The author did not calculate any formation constant from his experimental data, the equilibrium constant was calculated by this review (appendix A).

[b] The extrapolation to zero ionic strength or ionic strength correction was performed by this review (by using the SIT).

[c] The author interpreted his experimental results with other chemical equilibria. The equilibrium constant tabulated here was then calculated by this review (appendix A).

[d] The author did not use the speciation: he wrote the equilibrium as Np(VI) + e^- ⇔ Np(V).

[e] This uncertainty given by the author should be increased for junction potential and possibly calibration of the reference electrode (appendix A).

[f] This constant is calculated by this review from data given by the author.

[g] This value was calculated by the author; but he finally considered that there was no evidence of the corresponding species.

[h] Probably room temperature

[i] Corrected by this review for the dissociation of the Np(V) limiting complex

[j] This data was used to obtain (or is) the standard values selected by this review

[k] $\varepsilon(NpO_2(CO_3)_2^{-2},Na^+) = \varepsilon(UO_2(CO_3)_2^{-2},Na^+) = -0.02 \pm 0.09\ kg.mol^{-1}$ [95SIL/BID] was used

Table VI.b: Possible maximum values of formation constants. It was not demonstrated that the species whose formation constants are here tabulated, were formed. Moskvin also proposed $NpO_2(OH)_2CO_3^{-2}$ and $(NH_4)_2NpO_2(OH)_2CO_3^{-2}$ formation constants; but his interpretation was completely in error. This review reinterpreted that experimental work quantitatively with other species (see Table VI.a and the discussion on [71MOS5] in the Appendix A). So those $NpO_2(OH)_2CO_3^{-2}$ and $(NH_4)_2NpO_2(OH)_2CO_3^{-2}$ species were rejected. Pratopo's interpretation and measurements were rejected (see the discussion on [93PRA/MOR, 95MOR/PRA] in the Appendix A).

medium	t(°C)	method	$\log_{10}K$	reference
$NpO_2(CO_3)_3^{-4} + 7/3\ H_2O \Leftrightarrow 7/3\ H^+ + 3\ CO_3^{-2} + 1/3\ (NpO_2)_3(OH)_7^-$				
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm	25	pot	62.35 ± 1.50	[84MAY][b]
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm	25	pot	<63.33	[84MAY][a]
$NpO_2(CO_3)_3^{-4} + 8/3\ H_2O \Leftrightarrow 8/3\ H^+ + 3\ CO_3^{-2} + 1/3\ (NpO_2)_3(OH)_8^{-2}$		pot		
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm	25	pot	<55.45	[84MAY][ac]
$3\ NpO_2(CO_3)_3^{-4} + 3\ H_2O \Leftrightarrow 8\ CO_3^{-2} + 3\ H^+ + (NpO_2)_3CO_3(OH)_3^+$				
1 M $NaClO_4$, $NaHCO_3$ $10^{-3.5} \leq P_{CO_2} \leq 0.028$atm	25	pot	<75.42	[84MAY][a]

[a] Maximum possible value estimated by this review from the data of the corresponding reference

[b] This value was calculated by the author; but he finally considered that there was no evidence of the corresponding species.

[c] The corresponding species was recently proposed only for Uranium [PAL/NGU].

Table VIc: Redox potential of the $NpO_2(CO_3)_3^{-5} \Leftrightarrow NpO_2(CO_3)_3^{-4} + e^-$ equilibrium measured in Na_2CO_3 aqueous solutions from 5 to 60°C. All the data are from [95OFF/CAP]. t is temperature (°C).

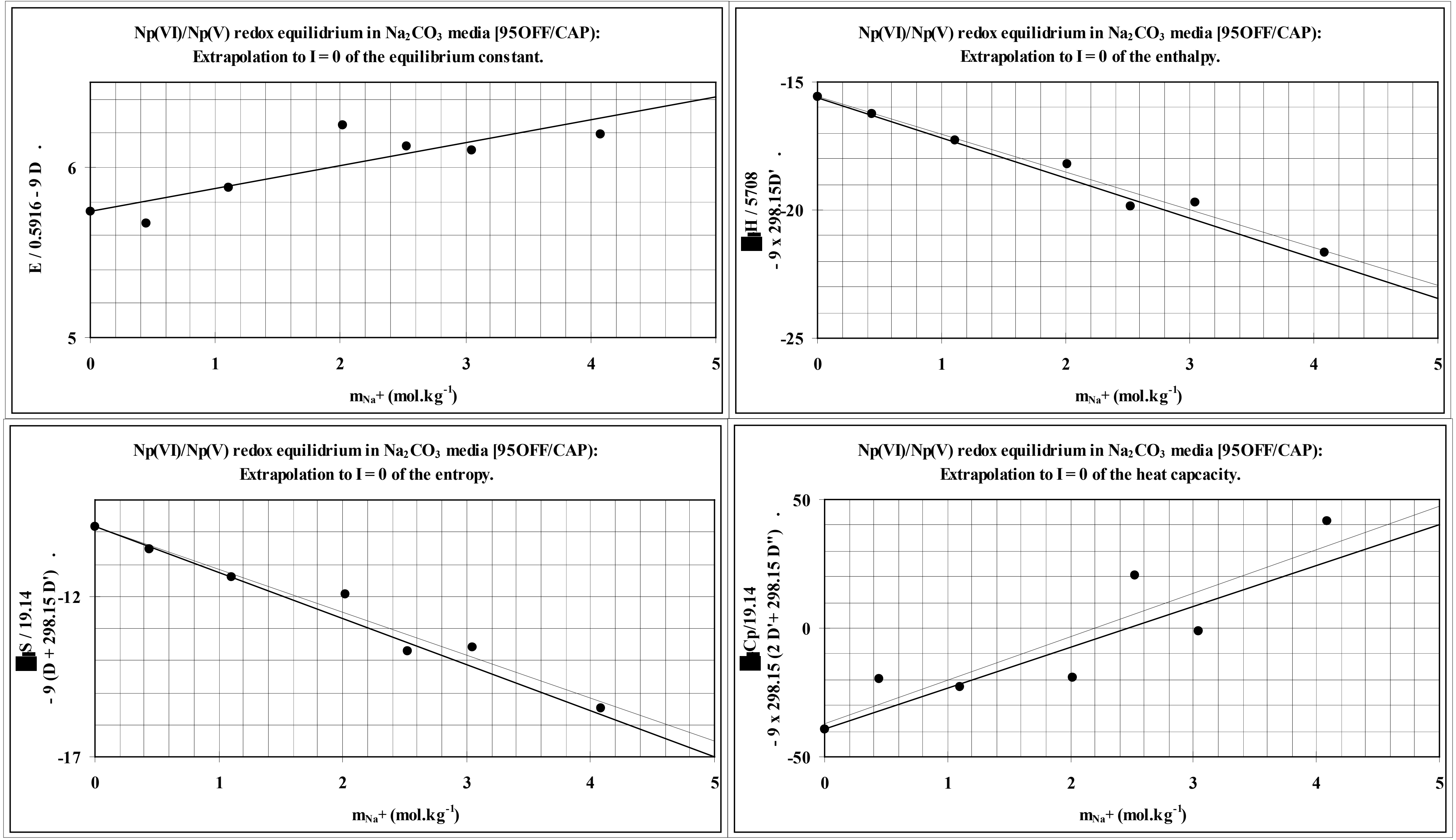
t	0[b]	0.22 M	0.55 M	1 M	1.25 M	1.5 M	2 M	$\Delta\varepsilon$(kg.mol^{-1})[b]
5	$0.374_4 \pm 0.016_3$	0.464_6	$0.500_0 \pm 0.004_2$	$0.533_8 \pm 0.001_4$	$0.538_8 \pm 0.001_4$	$0.539_7 \pm 0.002_3$	0.560_7	$0.26_6 \pm 0.06_3$
10							0.542_3	
15	$0.356_8 \pm 0.014_2$	$0.452_1 \pm 0.001_4$	$0.482_2 \pm 0.002_8$	$0.516_4 \pm 0.002_8$	$0.521_9 \pm 0.002_8$	$0.521_7 \pm 0.004_2$	$0.540_3 \pm 0.004_2$	$0.21_7 \pm 0.05_0$
25	$0.341_6 \pm 0.013_1$	$0.434_4 \pm 0.004_1$	$0.467_1 \pm 0.001_0$	$0.500_2 \pm 0.002_4$	$0.500_3 \pm 0.009_0$	$0.498_0 \pm 0.005_5$	$0.507_1 \pm 0.009_5$	$0.12_1 \pm 0.04_3$
(a)	$0.340_3 \pm 0.002_3$							0.13 ± 0.09
35	$0.320_1 \pm 0.019_9$	0.417_6	$0.451_3 \pm 0.001_4$	$0.483_4 \pm 0.004_2$	$0.470_3 \pm 0.004_2$	$0.479_0 \pm 0.006_3$	$0.483_8 \pm 0.001_4$	$0.07_9 \pm 0.06_5$
45	$0.294_8 \pm 0.013_1$	$0.400_5 \pm 0.002_0$	$0.431_0 \pm 0.004_2$	$0.461_3 \pm 0.002_8$	$0.453_0 \pm 0.002_8$	$0.455_8 \pm 0.004_2$	$0.465_9 \pm 0.001_9$	$0.06_5 \pm 0.03_9$
55	$0.270_5 \pm 0.018_3$	$0.381_2 \pm 0.001_4$	$0.410_2 \pm 0.006_9$	$0.443_2 \pm 0.002_8$	$0.445_8 \pm 0.002_8$	$0.438_3 \pm 0.001_1$	$0.449_4 \pm 0.004_2$	$0.07_1 \pm 0.05_6$
60	$0.287_6 \pm 0.020_0$			$0.433_9 \pm 0.001_4$	0.436_0	0.430_1	$0.438_5 \pm 0.001_4$	$-0.07_1 \pm 0.05_1$

(a)Results of t polynomial regression (to the second degree) about 25°C of the data measured at 5 to 55°C. The other results of E° polynomial regressions, are in the tableVIc, and are $\Delta\varepsilon = 0.12_9 \pm 0.02_6$ .kg.mol^{-1}, $\Delta\varepsilon' = -5.2_8 \pm 1.0_0$ g.mol^{-1},K^{-1} and $\Delta\varepsilon'' = 0.10_7 \pm 0.05_7$ g.mol^{-1},K^{-2} as calculated by this review from Offerlé's data [95OFF/CAP], here original determinations were 0.15 ± 0.05 kg.mol^{-1}, -5 ± 0.1 g.mol^{-1},K^{-1} and 0.02 g.mol^{-1},K^{-2} respectively. Uncertainty is 1.96σ on (too few) experimental data, actual uncertainty is rather the uncertainty on the value extrapolated to I=0.

(b)SIT extrapolation to I=0 from the data of the same line, uncertainty is 1.96σ on this regression.

Table VId: Δ_rH_m, Δ_rS_m and Δ_rCp_m at 25°C for the $NpO_2(CO_3)_3^{-5} \Rightarrow NpO_2(CO_3)_3^{-4} + e^-$ reaction in Na_2CO_3 aqueous solutions, deduced from redox potential measurements from 5 to 55°C. These values were recalculated by this review from Offerlé's data [95OFF/CAP]. Here original values are in the lines [95OFF/CAP].

[Na2CO3] (M)		E (V/SHE)	lgK	Δ_rG (kJ.mol.$^{-1}$)	Δ_rH(kJ.mol.$^{-1}$)	Δ_rS(J.mol.$^{-1}$K^{-1})	Δ_rCp(J.mol.$^{-1}$K^{-1})
	0	$0.340_3 \pm 0.002_3$	$5.75_1 \pm 0.03_9$	$-32.8_3 \pm 0.2_2$	$-88._{77} \pm 2._{93}$	$-187._6 \pm 9._7$	-759 ± 141
[95OFF/CAP]	0	$0.336_2 \pm 0.009_4$				-190 ± 5	-345 ± 750
	0.22	$0.434_8 \pm 0.002_7$	$7.35_0 \pm 0.04_5$	$-41.9_5 \pm 0.2_6$	$-88._{73} \pm 0._{91}$	$-156._9 \pm 3._0$	-304 ± 86
[95OFF/CAP]	0.22					-159	-305
	0.55	$0.467_4 \pm 0.003_3$	$7.90_0 \pm 0.05_6$	$-45.0_9 \pm 0.3_2$	$-94._{16} \pm 1._{18}$	$-164._6 \pm 3._9$	-352 ± 112
[95OFF/CAP]	0.55					-164	-355
	1	$0.500_1 \pm 0.002_7$	$8.45_4 \pm 0.04_6$	$-48.2_5 \pm 0.2_6$	$-99._{06} \pm 0._{93}$	$-170._4 \pm 3._1$	-282 ± 87
[95OFF/CAP]	1	0.504_5				-169	-235
	1.25	$0.497_1 \pm 0.010_1$	$8.40_2 \pm 0.17_1$	$-47.9_6 \pm 0.9_8$	$-108._{42} \pm 2._{81}$	$-202._8 \pm 9._4$	475 ± 329
[95OFF/CAP]	1.25					-200	515
	1.5	$0.498_6 \pm 0.004_5$	$8.42_8 \pm 0.07_6$	$-48.1_1 \pm 0.4_4$	$-107._{53} \pm 1._{00}$	$-199._3 \pm 3._3$	64 ± 124
[95OFF/CAP]	1.5					-197	128
	2	$0.507_9 \pm 0.007_6$	$8.58_6 \pm 0.12_9$	$-49.0_1 \pm 0.7_4$	$-118._{71} \pm 2._{48}$	$-233._8 \pm 8._3$	891 ± 262
[95OFF/CAP]	2					-230	758



Figures VI-7: Extrapolation to zero ionic strength of the normal potential, the enthalpy, entropy and heat capacity changes at 25°C from the redox potential measured by Offerlé [95OFF/CAP] at different temperatures in Na_2CO_3 media. The points are obtained by fitting normal potential experimental results as a function of (T-T°) with second order polynomial function (T° = 298.15 K). Thin line are SIT linear regression, thick lines are predictions using the fitting results Δε(T°), Δε'(T°) and Δε"(T°) values (figure VI-5).

Appendix A

Np(VI) in carbonate media: draft proposed for the TDB review by Pierre Vitorge.

[65IAK/GOR]

Iakolev G.N., Gorbeko-Germanov D.S. *Coprécipitation de l'américium(V) avec les carbonates doubles d'uranium(VI), ou de plutonium(VI) avec le potassium.* In French, Conf. sur l'utilisation pacifique de l'énergie nucléaire. Genève. Séance P/677(U.R.S.S.) (1965) 355-358.

The pale green solid $K_4PuO_2(CO_3)_{3(s)}$ is prepared by oxidising a 0.017 M Pu (certainly Pu(IV)) aqueous solution in concentrated K_2CO_3 media at 95 to 100°C during 15 to 20 minutes. Its stoichiometry is determined by chemical analysis. Its X-ray diffraction pattern is found to be similar to the known $K_4UO_2(CO_3)_{3(s)}$ one. No thermodynamic data can be deduced from this work; but one of the authors has contributed later [66GOR/KLI] to solubility measurements of the same type of solid phases, from which this review deduced equilibrium constants.

[66GOR/KLI]

Gorbeko-Germanov D.S., Klimov V.C. *Potassium dioxotricarbonato-neptunate(VI).* Russian J. Inorg. Chem. (1966) 11, 3, 280-282

$K_4NpO_2(CO_3)_{3(s)}$ is prepared and chemically analysed in the same way as $K_4PuO_2(CO_3)_{3(s)}$ [65IAK/GOR]. The authors say that its X-ray diffraction pattern is similar to the $Na_4UO_2(CO_3)_{3(s)}$ one. The initial solid was then assumed well characterised. Its solubility was measured at 20±2°C in 0, 0.2, 1 M and 50% K_2CO_3 (probably 50 % anhydrous solute weight percentage corresponding to 5.573 M aqueous solutions). Solubility decreases with initial K_2CO_3 concentration, this might be attributed to $[K^+]$ increase in solution due to the following reaction

$$K_4NpO_2(CO_3)_{3(s)} \Rightarrow NpO_2(CO_3)_3^{4-} + 4\ K^+$$

since it is now well established that in concentrated carbonate aqueous solutions, the major Np(VI) soluble complex is $NpO_2(CO_3)_3^{4-}$. Still, ionic strength effect cannot be neglected in this medium and the stoichiometry of the major soluble complex cannot then be determined from only this work (for the same reason, the analogy with the well documented [92GRE/FUG] $Na_4UO_2(CO_3)_{3(s)}$ solid could be only qualitative: see below). Nevertheless, this review calculated the constant of the above equilibrium as follows.

Using the formation constant of $NpO_2(CO_3)_3^{4-}$ and the other equilibrium constants selected in this review, we first checked, that all the other soluble complexes can be disregarded in the conditions of this study. This review calculated the speciation of the carbonate anions assuming either closed system, either equilibrium with the air (see also [95VIT]): $CO_{2(g)}$ penetration in the solution has negligible effect on the above equilibrium in the conditions of this study. Since the authors measured the solubility after dissolving $K_4NpO_2(CO_3)_{3(s)}$, $[K^+]$ was estimated as follows

$$[K^+] \approx 2\ [K_2CO_3]_i + 4\ [Np(VI)]_t$$

The experimental information given in the publication is $[K_2CO_3]_i$, the concentration of K_2CO_3 before $K_4NpO_2(CO_3)_{3(s)}$ addition, and $[Np(VI)]_t$, the measured solubility. This review calculated (figure [66GOR/KLI])

$\varepsilon(NpO_2(CO_3)_3^{4-},K^+) = -0.62 \pm 0.42$

to be compared with $\varepsilon(NpO_2(CO_3)_3^{4-},NH_4^+) = -0.78 \pm 0.25$ [71MOS5] in this Appendix,

(selected in this series) $\varepsilon(UO_2(CO_3)_3^{4-},Na^+) = -0.01 \pm 0.11$ [92GRE/FUG][95SIL/BID],

(from $Na_4UO_2(CO_3)_{3(s)}$ solubility) $\varepsilon(UO_2(CO_3)_3^{4-},Na^+) = -0.13 \pm 0.07$ [92GRE/FUG].

(uncertainties is deduced from 1.96 σ on $\Delta\varepsilon = 0.54 \pm 0.37$ calculated from the slope of the SIT regression), and this review calculated the value of the standard equilibrium constant

for $K_4NpO_2(CO_3)_{3(s)}$ $\log_{10}Ks_3 = -7.03 \pm 0.88$ for comparison

for $Na_4UO_2(CO_3)_{3(s)}$ $\log_{10}Ks_3 = -5.34 \pm 0.16$ [92GRE/FUG]

The uncertainty is deduced from the standard deviation to which this review added the uncertainty for possible systematic error on $\log_{10}[K^+]$ (0.1 $\log_{10}$ unit) because it had to be deduced (nearly guess) from the original data.

Table [66GOR/KLI]: Calculation of Ks_3, the constant of the $K_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ K^+$ equilibrium. Data are tabulated in molar unit, except for Δε (kg/mol.). ρ (dm^3/kg) is the factor used for the conversion of molarity to molality. Calculations are also performed assuming precipitation of $K_4NpO_2(CO_3)_{3(s)}$; but the authors certainly used dissolution. ε and 0 ionic strength values are the results of the SIT regressions; where the values at $[K_2CO_3]_i$ too high for the SIT approximation (5.573 M in italic face) are not taken into account. $\log_{10}Ks_{3th}$ are the theoretical values recalculated according to the SIT. The uncertainties are 1.96 σ, 0.1 is added for possible systematic error on $\log_{10}[K^+]$, so 0.4 on $\log_{10}Ks_3$ (see text). The interpretation of this publication proposed by this review is printed in bold face.

Experimental data		Calculation assuming: dissolution				or precipitation		
		$\Delta\varepsilon=-0.538\pm0.367$ $\log_{10}Ks_3°=-7.033\pm0.876$					$\Delta\varepsilon' = -0.818$	
$[K_2CO_3]_i$	$\log_{10}[S]$	$[K^+]$	$\log_{10}Ks_3$	ρ	$\log_{10}Ks_{3th}$	ρ'	$\log_{10}Ks_3'$	$\log_{10}Ks_{3th}'$
		0			**-7.033**			-7.161
0	-0.943	0.456	**-2.308**	1.017	-2.484			
0.2	-1.606	0.499	**-2.813**	1.014	-2.632	1.010	-3.198	-3.198
1	-2.083	2.033	**-0.851**	1.053	-0.855	1.039	-0.879	-0.879
5.573	-4.083	11.146	***0.105***	1.324	6.341	1.008	*0.105*	7.679
		Including the data at $[K_2CO_3]_i$ = 5.573 M, in the SIT regression:						
		$\Delta\varepsilon=-0.089 \pm 0.039$, $\log_{10}Ks_3 = -6.588 \pm 0.292$				$\Delta\varepsilon'=-0.076\pm0.108$, $\log_{10}Ks_3' = -6.293\pm0.710$		

Table [71MOS5]-1: Calculation of the constant of the $(NH_4)_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ NH_4^+$ equilibrium, Ks_3. Molar unit data are tabulated for concentrations. ρ (dm^3/kg) is the factor used for the conversion of molarity to molality. Calculations are performed assuming dissolution of the starting solid: either $(NH_4)_4NpO_2(CO_3)_{3(s)}$ (upper part of the table) or of $NpO_2(OH)_{2(s)}$ (bottom part of the table).

Experimental data		Our interpretation		
$[(NH_4)_2CO_3]_i$	$\log_{10}[S]$	$[NH_4^+]$	$\log_{10}Ks_3$	ρ
Starting material: $(NH_4)_4NpO_2(CO_3)_{3(s)}$;		$(NH_4)_4NpO_2(CO_3)_{3(s)}$ is assumed to control the solubility$^{(1)}$		
0	-0.975	0.245	-3.419	1.019
0.1	-1.184	0.267	-3.482	1.017
0.5	-1.646	0.674	-2.332	1.032
0.75	-1.796	0.985	-1.822	1.046
1	-1.896	1.311	-1.426	1.060
1.25	-2.053	1.639	-1.195	1.074
1.5	-2.080	1.979	-0.895	1.090
1.8	-2.177	2.389	-0.664	1.108
2.2	-2.346	2.942	-0.471	1.134
The starting material was $NpO_2(OH)_{2(s)}$;		but it certainly did not controlled the solubility		
0.25	-1.735	0.299	-3.831	1.016
0.3	-1.714	0.362	-3.480	1.019
0.45	-1.670	0.553	-2.698	1.028
0.6	-1.674	0.748	-2.179	1.037
The starting material was $NpO_2(OH)_{2(s)}$;		but $(NH_4)_4NpO_2(CO_3)_{3(s)}$ certainly controlled the solubility$^{(1)}$		
0.75	-1.807	0.945	-1.905	1.045
1	-1.876	1.278	-1.450	1.059
1.25	-2.085	1.616	-1.251	1.074

(1)Data used for SIT regressions in the [71MOS5]-2 table

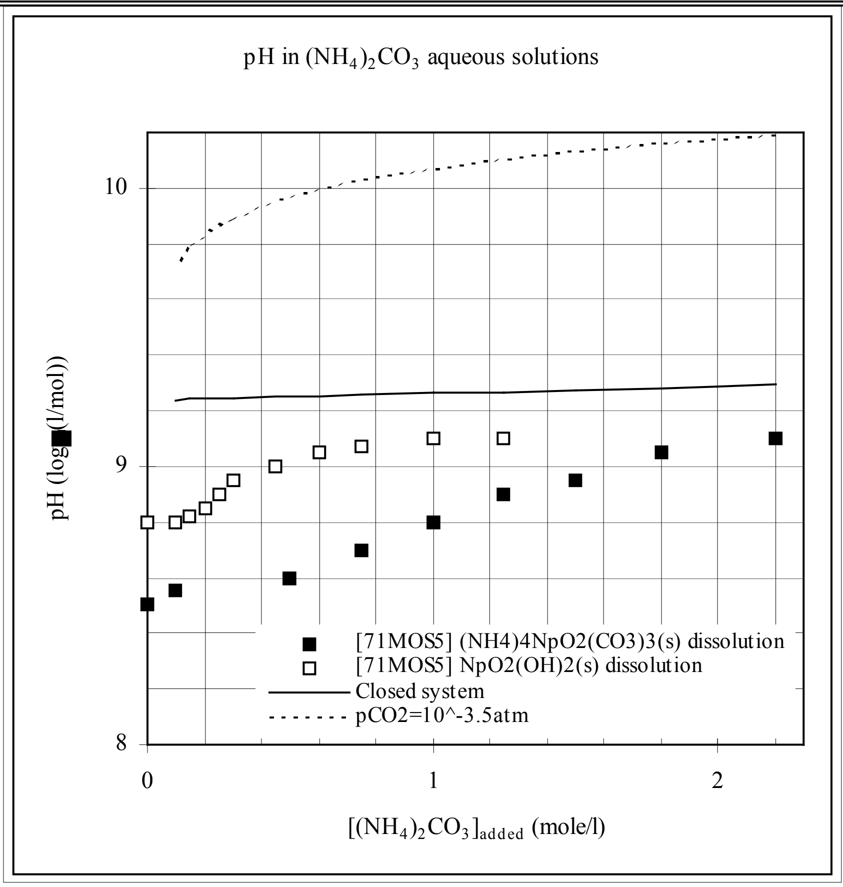


Figure [71MOS5]-1 pH in $(NH_4)_2CO_3$ aqueous solutions. The pH calculated in closed system lead to a carbonic gas partial pressure higher than in the air: this explains the relative position of the calculated curves (lines). This medium is buffered by the CO_3^{2-}/HCO_3^- and NH_3/NH_4^+ couples. The difference between their pK_a values is small and depends on the ionic strength.

$\log_{10}Ks_3°$ here calculated for the neptunium-potassium equilibrium, is smaller than the corresponding uranium sodium one; but this comparison relies on the values attributed to the activity coefficients. The $\varepsilon(NpO_2(CO_3)_3^{4-},K^+)$ value calculated here is similar to the $\varepsilon(NpO_2(CO_3)_3^{4-},NH_4^+)$ value calculated by this review (in this appendix) from the reference [71MOS5]; but is quite different from the $\varepsilon(UO_2(CO_3)_3^{4-},Na^+)$ value selected in this series [95SIL/BID], or determined [92GRE/FUG] from $Na_4UO_2(CO_3)_{3(s)}$ solubility in $NaClO_4$ media: ionic strength effects might not be exactly the same when Na^+ is exchanged for K^+ or along the actinide series (see also the discussion on [71MOS5, 77SIM and

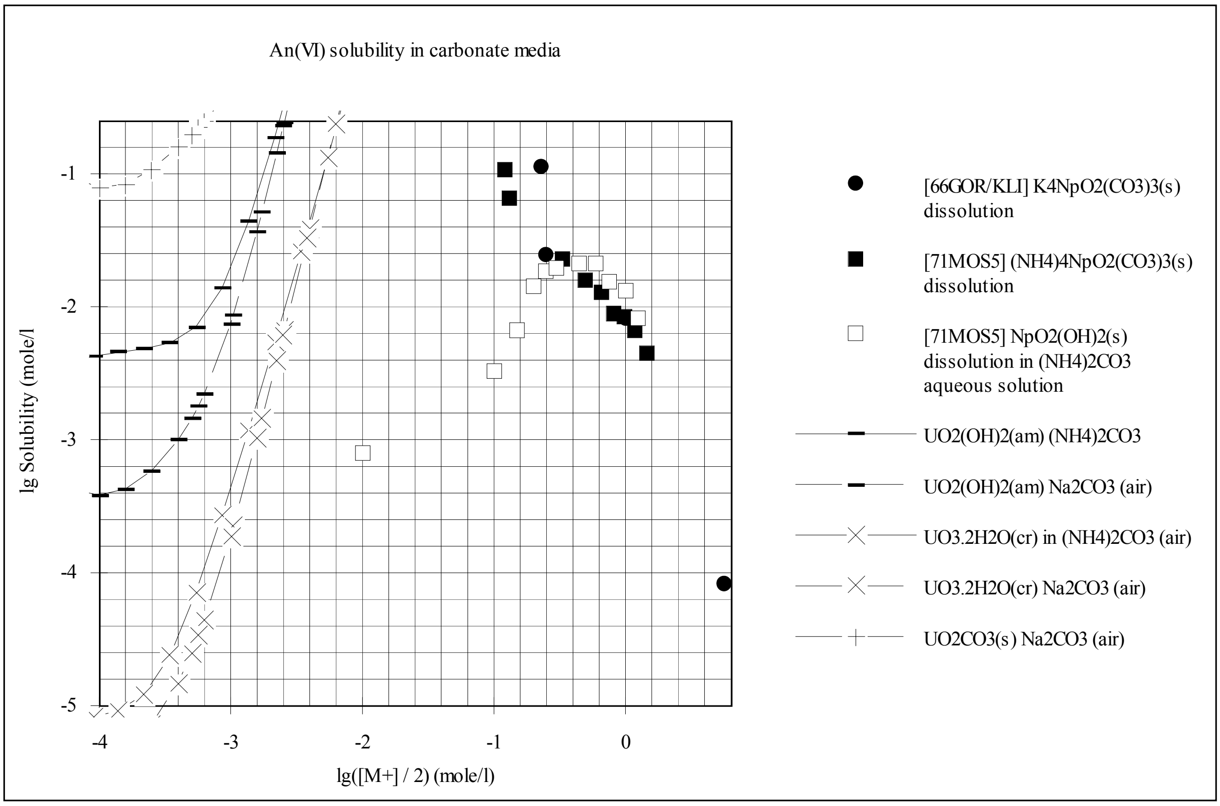


Figure [71MOS5]-2: U(VI) and Np(VI) solubility in some concentrated carbonate media the white square point plotted at $\log_{10}[NH_4^+]=-2$, where obtained at $[NH_4^+]=0$. The points are from the table [71MOS5]-1, the curves are calculated with the constant selected in [92GRE/FUG] and [95BID/SIL], in most cases (air) assuming equilibration with air.

95OFF/VIT] in this Appendix). Despite this small difference, this is the first experimental work that confirms chemical analogy between U(VI) and Np(VI) chemistry in concentrated carbonate media.

[71MOS5]

Moskvin, A.I. *Complex formation of neptunium(IV, V, VI) in carbonate solutions*. Radiokhimiya, 13(5) (1971) 674-681, in Russian; Engl. transl.: Sov. Radiochem., 13 (5) (1971) 694-699

The solubility of Np(VI) was measured by dissolving in $(NH_4)_2CO_3$ aqueous solutions, the $(NH_4)_4NpO_2(CO_3)_{3(s)}$ solid phase, and in another set of measurements, by dissolving the $NpO_2(OH)_{2(s)}$ one. There is very little experimental information and the interpretation given by the author is not consistent with later work (see the corresponding chapter) and with the chemical analogues (U(VI), Pu(VI)). As in the rest of the [71MOS5] publication, the author ignores that the free carbonate concentration is not the total one, and he does not try to show that the interpretation he gives is the only possible one, and that it could explain the published chemical information on this type of systems. The incorrect stoichiometry of Np(VI) soluble complexes, $NpO_2(OH)_2CO_3^{-2}$, $(NH_4)_2NpO_2(CO_3)_2$, proposed in this publication has to be suppressed, and the value of the equilibrium constant involving the $NpO_2(CO_3)_2^{-2}$ soluble complex is erroneous. This experimental work confirms chemical analogy between U(VI) and Np(VI) chemistry in carbonate media when it is correctly reinterpreted, this was already known (see the discussion on [66GOR/KLI] in this Appendix). The comparison between the solubility results and the amount of $(NH_4)_2CO_3$ used in these measurements, indicates that the amount of carbonate or ammonium ions due to the Np(VI) solid dissolution, can be disregarded (except when no $(NH_4)_2CO_3$ at all was added): speciation, except for Np(VI), is nearly the same before and after the Np(VI) solid dissolution (note that this approximation is less valid when calculating the solubility product where $[NH_4^+]^4$ is involved). This review then calculated the speciation in the same way as already explained [95VIT] for the data on Np(IV) of this publication. As for the other parts of this publication, the measured pH does not correspond to the theoretical value calculated by this review (figure [71MOS5-1]). There is no experimental indication on pH measurement (calibration, junction potential neither activity coefficient) in this publication. The two sets of experiments do not have the same pH for the same initial $(NH_4)_2CO_3$ concentration; this deviation is probably due to some experimental systematic error. As for the reviewing of the Np(IV) part of that publication, calculated speciation (and not pH measurements) was used for the reinterpretation of this work. This procedure could induce systematic error that has been included in uncertainty estimation.

Both sets of measurements in more than 0.5 M $(NH_4)_2CO_3$ aqueous solutions finally give the same solubility, whatever was the starting material, and it is the same solubility as the previously published one [66GOR/KLI] in K_2CO_3 aqueous solutions (figure (71MOS5]-2). The simplest and most consistent interpretation is then to assume that, in opposition to the interpretation of the [71MOS5] author, the solubility of the corresponding data was controlled by the

$$(NH_4)_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ (NH_4)^+$$

equilibrium. This review then performed the same interpretation as for [66GOR/KLI] in the present Appendix. The results of Ks_3 estimation (table [71MOS5]-1) and those of SIT regressions (table [71MOS5]-2), give the same values as in K^+ media (estimated in this Appendix from [66GOR/KLI]) within the uncertainty (K^+ and NH_4^+ are indeed usually found to be

Table [71MOS5]-2: Comparison of the constant of the $M_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ M^+$ equilibrium, Ks_3 in several media. ε (kg/mol.) and 0 ionic strength values are the results of SIT regressions, using the data of the tables [71MOS5]-1 and [66GOR/KLI]. The random part of the uncertainty (see text) on $\log_{10}Ks_3°$ is 1.96σ for the total uncertainty, 1.6 $\log_{10}$ unit was added as in the table [66GOR/KLI]. The interpretation of these publications proposed by this review is printed in bold face.

$\log_{10}Ks_3°$	±	Δε	±	ε	±	M^+	Data taken into account
-7.033	**0.876**	**0.538**	**0.367**	**-0.618**	**0.418**	**K^+**	[66GOR/KLI]
-7.513	0.660	0.713	0.172	-0.793	0.263	NH_4^+	[71MOS5] $(NH_4)_4NpO_2(CO_3)_{3(s)}$
-7.188	0.638	0.563	0.188	-0.643	0.274	NH_4^+	[71MOS5] $NpO_2(OH)_{2(s)}$ starting phase
-7.443	**0.608**	**0.695**	**0.144**	**-0.775**	**0.247**	**NH_4^+**	[71MOS5] all data in NH_4^+ media
-7.330	0.604	0.642	0.144	-0.722	0.247		all data in NH_4^+ and K^+media

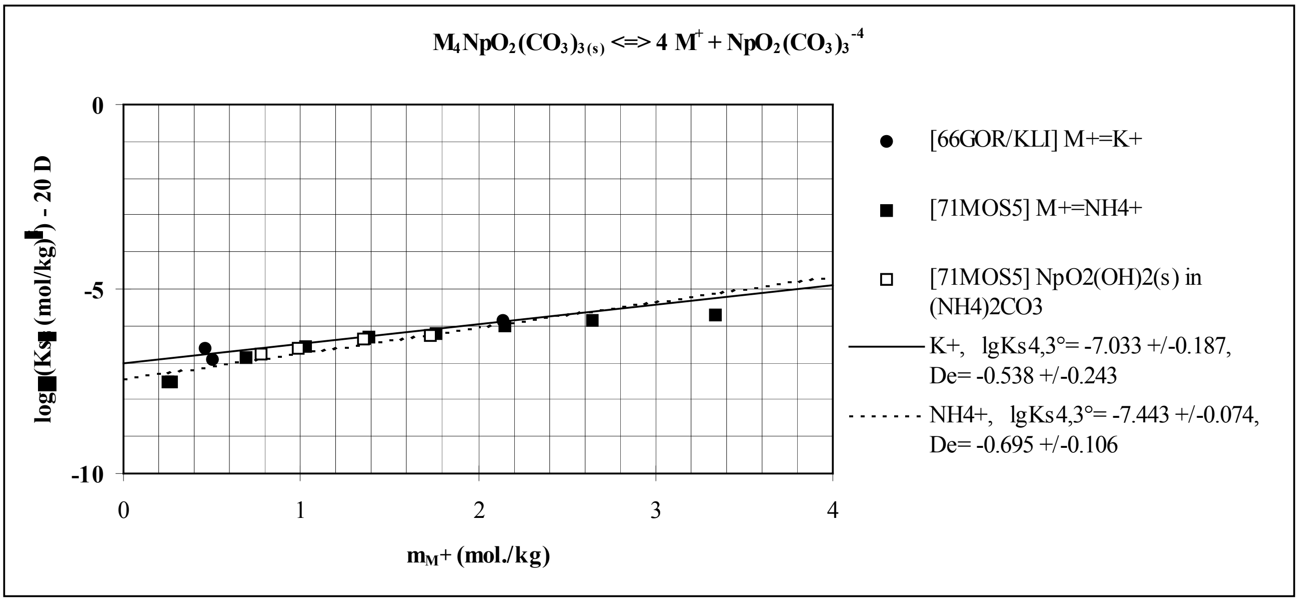


Figure [71MOS5]-3 Comparison of the constant of the $M_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ M^+$ equilibrium, Ks_3 in several media. $M^+ = K^+$ or NH_4^+. The points are from the tables [71MOS5]-1 and [66GOR/KLI]. $\log_{10}Ks_3$ - 20 D is plotted as a function of the total concentration of M^+. Ks4,3 is Ks_3. +/- is 1.96 σ. SIT regressions give $\log_{10}Ks_3°$ and Δε indicated on the figure and the corresponding plotted straight lines. For the data proposed by this review, see the corresponding chapter.

similar cations):

for $K_4NpO_2(CO_3)_{3(s)}$ $\log_{10}Ks_3°$ $= -7.03 \pm 0.88$

for $(NH_4)_4NpO_2(CO_3)_{3(s)}$ $\log_{10}Ks_3°$ $= -7.44 \pm 0.61$ to be compared with

for $Na_4UO_2(CO_3)_{3(s)}$ $\log_{10}Ks_3°$ $= -5.34 \pm 0.16$ [92GRE/FUG]

$\varepsilon(NpO_2(CO_3)_3^{4-},K^+) = -0.62 \pm 0.42$

$\varepsilon(NpO_2(CO_3)_3^{4-},NH_4^+) = -0.78 \pm 0.25$ to be compared with

(selected in this series) $\varepsilon(UO_2(CO_3)_3^{4-},Na^+) = -0.01 \pm 0.11$ [92GRE/FUG][95SIL/BID],

(from $Na_4UO_2(CO_3)_{3(s)}$ solubility) $\varepsilon(UO_2(CO_3)_3^{4-},Na^+) = -0.13 \pm 0.07$ [92GRE/FUG].

Uncertainty is deduced from statistical analysis after ionic strength corrections: this gives an estimate of 0.66 $\log_{10}$ unit for the random part of the uncertainty. As for the interpretation of [66GOR/KLI], this review added 4 x 0.4 $\log_{10}$ unit for possible systematic error on the speciation. Finally it was checked again whether any known soluble complex of Np(VI) could contribute to the solubility in the experimental conditions of this publication: a few per cent of the $(NpO_2)_3(CO_3)_3^{6-}$ could contribute to the solubility (this is a rough estimation since its activity coefficient value is estimated) in the less concentrated solutions, this should be less than the uncertainty.

No realistic thermodynamic interpretations could be find to account for the other solubility data obtained by dissolving the $NpO_2(OH)_{2(s)}$ solid phase (when the measured solubility was not the same as in the experiments where $(NH_4)_4NpO_2(CO_3)_{3(s)}$ was used as starting material). None of them gave results consistent with the other chemical information on actinide(VI) system in aqueous carbonate media (figure [71MOS5]-2). This means that the corresponding data might be an evidence of a new solid phase containing less carbonate than $(NH_4)_4NpO_2(CO_3)_{3(s)}$; but it can simply be interpreted by a slow dissolution process of the initial Np(VI) compound. No further quantitative interpretation of those data is then tried.

[73KHA/MOS]

Kharitonov Y.Y., Moskvin, A.I. *IR absorption spectra of some neptunium compounds. III. carbonate compounds.* Radiokhimiya, 15 (2) (1973) 246-249, in Russian; Engl. transl.: Sov. Radiochem., 15 (2) (1973) 240-243

This publication was not used in the present review.

Table [74SIM/VOL]: Redox potential of the An(VI)/An(V) couples measured in K_2CO_3 aqueous solutions Concentration is in mol./l. The data and uncertainty (0.01 V) are those given by the author.

	$[K_2CO_3]$	E		$[K_2CO_3]$	E		$[K_2CO_3]$	E
Np	0.2	0.43	Pu	0.1	0.3	Am	1	0.9
	0.8	0.44		1	0.32			
	3	0.44						

Table [75SIM]: Normal potential of the Np(VI) + e⁻ ⇔ Np(V) equilibrium in different media. T = 25°C. N is the normality, it is then the total concentration of $HClO_4$, and it would be 2M in H_2SO_4 or Na_2CO_3 solution; but this definition of normality was probably not used for Na_2CO_3 since in a later work [77SIM] it seems that the same measurement corresponds to 1 M Na_2CO_3. E is the normal potential. ΔE is the potential shift compared to 1 N non complexing medium: ΔE = E - E(in 1 M $HClO_4$). The E, ΔE and uncertainty values tabulated here are those given by the author. This review has increased uncertainty to 0.05 V (see the text). In Na_2CO_3 media, $\Delta E/0.05916 = \log_{10}(\beta_3(VI) / \beta_3(V))$.

Data from table 1 of [75SIM]					Our calculations	
	mol./l N	V/N.H.E. E	V ±	pH	V ΔE	ΔE/0.05916
$HClO_4$	1	1.17	0.01			
$HClO_4$	0.1	1.18	0.01			
H_2SO_4	1	1.09	0.01		-0.08	1.352
Na_2CO_3	1	0.46	0.01	11.5	-0.71	12.00

[74SIM/VOL]

Simakin G.A., Volkov Yu.F., Visyashcheva G.I., Kapsukov I.I., Baklanova P.F., Yakovlev G.N. *Carbonate compounds of pentavalent actinides with alkali metal cations. II. Preparation of carbonate compounds of Np(V), Pu(V) and Am(V) from K_2CO_3 solution by electrochemical reduction.* Radiokhimiya, 16 (6) (1974) 859-863, in Russian; Engl. transl.: Sov. Radiochem., 16 (6) (1974) 838-841.

The authors doe not give enough experimental information to make an accurate interpretation of this work. Still it is quite clear that they have prepared the compounds indicated in the title. They checked that one electron was exchanged during the preparation. They deduced at 20 ± 1°C the normal redox potential plus the junction potential. The junction potential is probably less than the uncertainty. The Np(VI)/Np(V) potential shift from acidic to these carbonate media is

$$E_{Np(VI)/Np(V)\text{ in 1M }Na_2CO_3} - E_{Np(VI)/Np(V)\text{ in 1M }HClO_4} = -0.6 \text{ to } -0.7\text{ V}$$

according to the authors. This correspond to

$$\log_{10}(\beta_{3Np(VI)}/\beta_{3Np(V)})_{0.2\text{ to 3 M }K_2CO_3} = 11.2 \pm 0.9$$

since it is now know that the two limiting complexes are $NpO_2(CO_3)_3^{4-}$ and $NpO_2(CO_3)_3^{5-}$. See the discussion on [75SIM] and [77SIM] in this Appendix, for further quantitative interpretation and discussion of these data.

[75SIM]

Simakin, G.A. *Kinetic parameters of the electrochemical reaction $NpO_2^{2+} + e^- \Leftrightarrow NpO_2^+$ on a smooth platinum electrode in various media*, Elektrokhi., 11(7) (1975) 1026-30, English translation: Sov. Electrochem., 11(7) (1975) 947-9.

This is a careful work of the electrochemical equilibrium

$$Np(VI) + e^- \Leftrightarrow Np(V)$$

in $HClO_4$, H_2SO_4 and Na_2CO_3 aqueous solutions. The normal potentials reported in this publication are probably not corrected for junction potential. The experimental set up used seems to give relatively small junction potentials; but it is possibly more than the value of the uncertainty reported by the author (0.01 V). In a later study [77SIM] the same author estimates that the junction potential is less than 0.01 V in similar media; but the uncertainty could still be more than this value (see the discussion on [77SIM] in this appendix).

The value of the normal potential in non complexing medium 1.18±0.01 V/N.H.E. is not consistent (within the uncertainty estimated by the author) with the value selected in this review 1.14±0.01 V/N.H.E: the difference between the two values is 0.04 V. The discrepancy is probably due to some systematic error (junction potential, calibration of the reference electrode). The ΔE values

$$E_{Np(VI)/Np(V)\text{ in 1M }Na_2CO_3} - E_{Np(VI)/Np(V)\text{ in 1M }HClO_4} = -0.71 \pm 0.01_4\text{ V}$$

is also different (by at least 0.05 ± 0.03 V) from the value calculated with the thermodynamic data selected in this review. It is consistent with the previous measurement of the author [74SIM/VOL]

$$E_{Np(VI)/Np(V)\text{ in 1M }Na_2CO_3} - E_{Np(VI)/Np(V)\text{ in 1M }HClO_4} = -0.6 \text{ to } -0.7\text{ V}$$

Since enough reliable data in $HClO_4$ and Na_2CO_3 media are published elsewhere (see the corresponding chapters) these results could be simply rejected; but the value in carbonate medium can be kept increasing its uncertainty to at least 0.02 V, which is reasonable for the possible calibration systematic deviation indicated above. Finally, this review used an uncertainty of 0.05 V to be sure that it is more than the unknown junction potential. From this uncertainty and ΔE, this review calculated

$$\log_{10}(\beta_{3Np(VI)}/\beta_{3Np(V)})_{0.1\text{ to 2 M }Na_2CO_3\text{ or }K_2CO_3} = 12.0 \pm 1.2$$

to be compared with $\log_{10}(\beta_{3Np(VI)}/\beta_{3Np(V)})_{0.2\text{ to 3 M }K_2CO_3} = 11.2 \pm 0.9$ [74SIM/VOL]

The data proposed in this work, are consistent with those published by the same author earlier in similar carbonate media [74SIM/VOL] or later in similar or identical carbonate media [77SIM]; but it is 0.044 ± 0.017 V more than [95OFF/CAP] value published later. Later information by the same author on this subject [77SIM] allows an estimation of the calibration of his reference electrode (see the discussion of [77SIM] in this Appendix): it is over estimated by 0.021 V;

but the reference electrodes in [77SIM] and in [75SIM] were not the same, so this review did not correct the above value by 0.021 V. Nevertheless, this illustrates that the 0.05 V uncertainty estimated above, is reasonable.

[76SHI/STE]

Shilov, V.P., Stepanova E.S., Krot N.N. *Behaviour of Neptunium(VII) in carbonate solutions*, Radiokhimiya., 18(3) (1976) 350-4, English translation: Sov. Radiochem., 18(3) (1976) 350-4

This paper probably presents an evidence of the formation of a carbonate complex of Np(VII) in ≈ 0.5 M K_2CO_3 solutions at pH 6 to 10; but the stoichiometry of the complex is not determined.

[77SAI/UEN]

Saito, A., Ueno, K. *The precipitation of some actinide element complex ions by using hexammine cobalt(III) cation, V.: Absorption spectra and the precipitation of Np(IV), (V) and (VI) carbonate complex ions*, J. Inorg. Nucl. Chem., 39 (1977) 315-8.

Np(IV), (V) and (VI) are precipitated in 0.05 to 0.8 M Na_2CO_3 aqueous solutions by using hexammine cobalt(III) cation. The composition of the solid phase (or phases ?) are deduced from chemical analysis. Absorption spectra are shown for aqueous solutions containing Neptunium at each valence state.

For Np(VI), it is concluded that the solid contained the same proportion of Np and carbonate as in the $NpO_2(CO_3)_3^{4-}$ soluble complex, which his now known to be the major soluble complex in the conditions used by the authors. The solubility is then expected to be quite constant (only small variations due to ionic strength effects are expected); but the experimental results are in contradiction with this interpretation: the measured solubility is increased by two orders of magnitude in aqueous solutions when $[Na_2CO_3]$ is changed from 0.05 to 0.8 M. This could be due to the formation of an unknown intermediary or limiting soluble species possibly stabilised by the hexammine cobalt(III) cation (or a special ionic strength effect due to this big cation). This could also be due to kinetic effects. These results are then not used in this review.

[77SIM]

Simakin G.A. *Real oxidation potentials of the couples AmO_2^{2+}-AmO_2^{+}, NpO_2^{2+}-NpO_2^{+} in solutions of potassium and sodium carbonates.* Radiokhimiya, 19 (4) (1977) 518-521 Engl. transl.: Sov. Radiochem., 19 (4) (1977) 424-426

The redox potential of Np(VI)/Np(V) and Am(VI)/Am(V) couples were measured in 0.1 to 2 M Na_2CO_3 or K_2CO_3 aqueous solutions. The author estimated that the junction potential was less than 0.01 V; it seems that the author called junction potential, the overall calibration of the reference electrode: this review used this interpretation and found reliable results (see below), that then appeared to be consistent with the only other published measurements of the Np(VI)/Np(V) redox potential [95OFF/CAP] where the junction potential was explicitly taken into account. So this 0.01 V estimation of uncertainty is accepted: it is about the same value calculated by this review after SIT extrapolation to zero ionic strength (table [77SIM]-2). The author says that the uncertainty on each experiment is 0.001 V: uncertainty is mainly attributed to reproducibility of the reference electrode calibration.

It is confirmed [75SIM] that in these conditions the variations of the potential with $[CO_3^{2-}]$ are small, probably only due to junction potential and ionic strength effects: this interpretation of the author is correct. He then concludes that the limiting complexes of Np(V) and Np(VI) have the same carbonate stoichiometry: this is correct and confirmed by the analysis of later worker made in this review. The author then determined the stoichiometry of the limiting complex of Np(V) by measuring its solubility, S, at constant (and high) ionic strength: it was controlled by the $Na_3NpO_2(CO_3)_{2(s)}$ solid phase (the author said that it was identified by X-ray diffraction and for this identification acknowledged Yu. F. Volkov who indeed published on this subject). $\log_{10}S$ increases with a slope of 1 as a function of $\log_{10}[CO_3^{2-}]$. The authors then concluded that solubility was controlled by the

$$Na_3NpO_2(CO_3)_{2(s)} + CO_3^{2-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + Na^+$$

equilibrium, that the limiting complex of Np(V) is $NpO_2(CO_3)_3^{5-}$ and then that the limiting complex of Np(VI) is $NpO_2(CO_3)_3^{4-}$, which is correct and confirmed by the analysis of later worker made in this review. It is then the first evidence and correct interpretation of the stoichiometry of the carbonate limiting complexes of Np(V) and Np(VI) (but see the remark below).

Still, the author assumes, that only monomeric soluble complexes can be formed; but he did not demonstrate it, since he did not study the influence of the total Np concentration (solubility study with a unique solid phase, cannot detect polymerisation). Actually it is now recognised (in [92GRE/FUG] for uranium and in the present review for Np and Pu) that a polynuclear carbonate complex of actinide(VI), namely $(AnO_2)_3(CO_3)_6^{6-}$ can be stable in certain chemical conditions and this is clearly demonstrated for Np(VI) [86GRE/RIG, 89RIG]. Fortunately $(NpO_2)_3(CO_3)_6^{6-}$ is not a predominant species in the condition used here (in [77SIM]). It was also demonstrated later [89RIG] that not any Np(V) polymeric carbonate complex is stable (at least in these conditions): so the conclusion of the author is correct; but the actual demonstration of the stoichiometry of the limiting complex of Np(V) and Np(VI) was done only later.

The shifts of potential between these carbonate media and a non complexing one (1 M $HClO_4$) for all actinide(VI) is then reported to be about 0.7 V. This is of the correct order of magnitude (calculated from [92GRE/FUG] for uranium, this review for Np and Pu and [95SIL/BID] for Am) and this confirms the previous estimation made by the author [75SIM]; but more accurate estimation can now be performed (see the corresponding chapter).

Table [77SIM]-1: Redox potential of the Np(VI)/Np(V) couple measured in Na_2CO_3 and K_2CO_3 aqueous solutions reported in [77SIM] and previous works. E_j is called junction or diffusion potential by the author; but it is certainly the value of the potential of the calomel electrode (used as reference electrode during the measurements) versus an AgCl/Ag electrode with, in principle, low junction potential. E_j and the data graphically estimated on the figure 1 of this publication are used to calculate the normal potential, E, as explained in the text, this ends up with a systematic correction of 0.021 V. The data previously published by this author [75SIM] are also tabulated; but without this systematic correction. The data of this table are used to performed SIT regression in (table [77SIM]-2). ρ is the molar to molal conversion factor. This review assumed that there is an inversion between K_2CO_3 and Na_2CO_3 on the text of the figure 1 of this publication. E_c is E corrected for $NpO_2(CO_3)_3^{-5}$ dissociation.

	Table 1 of [77SIM]		Figure 1 of [77SIM]		Calculated by us			
	$[K_2CO_3]$	E_j	$\log_{10}[CO_3^{2-}]$	E(V/SCE)	E	E'_j	E_c	ρ
	0.1	0.036	-0.715	0.185	0.4460	-0.0053	0.4385	1.0073
	0.3	0.044	-0.295	0.185	0.4513	0.0000	0.4456	1.0193
	0.5	0.045$^{(a)}$	-0.11	0.185	0.4519	0.0006	0.4516	1.0296
	1	0.046	0.005	0.197	0.4644	0.0011	0.4642	1.0388
	1.5	0.05	0.185	0.202	0.4731	0.0048	0.4731	1.0593
	2	0.047	0.3	0.205	0.4733	0.0020	0.4733	1.0780
			0.405	0.207	0.4721	-0.0012	0.4720	1.1003
mean [77SIM]		*0.0447*		*0.1951*	*0.4614*	*0.0003*	*0.4598*	
σ		*0.0092*		*0.0195*	*0.0195*	*0.0061*	*0.0144*	
[74SIM/VOL]	0.2				0.43			1.0076
[74SIM/VOL]	0.8				0.44			1.0306
[74SIM/VOL]	3				0.44			1.1195
mean (all data)					*0.454*			
σ					*0.0231*			
	$[Na_2CO_3]$	E_j	$\log_{10}[CO_3^{2-}]$	E(V/SCE)	E	E'_j	E_c	ρ
	0.1	0.034	-0.88	0.18	0.4369	-0.0094	0.4214	1.0015
			-0.69	0.186	0.4465	-0.0058	0.4398	1.0024
	0.3	0.044	-0.515	0.193	0.4583	-0.0010	0.4555	1.0035
	0.5	0.043$^{(a)}$	-0.295	0.202	0.4664	-0.0019	0.4655	1.0059
			-0.132	0.208	0.4752	0.0009	0.4748	1.0085
	1	0.049	0.008	0.222	0.4923	0.0040	0.4922	1.0118
	1.5	0.05	0.185	0.228	0.4994	0.0051	0.4993	1.0178
	2	0.051	0.32	0.238	0.5105	0.0062	0.5105	1.0243
mean [77SIM]	*0.9000*	*0.0452*		*0.2071*	*0.4732*	*-0.0003*	*0.4699*	
σ		*0.0125*		*0.0407*	*0.0510*	*0.0107*	*0.0305*	
[75SIM]					0.46			1.0116
mean (all data)	*0.9143*				*0.4720*			
σ					*0.0441*			

$^{(a)}$this value is assumed (by this review) to reflect zero junction potential (E'_j=0).

The authors measured the difference of the potential between the saturated calomel electrode that they used here (its potential is usually assumed to be 0.244_4 V/E.N.H.) as a reference electrode, and an AgCl/Ag reference one (with possibly low junction potential): they found 0.044 V, which is 0.021 V more than the standard value used in the present review ($0.222_3 \pm 0.001_6$ V for the standard potential of the AgCl/Ag redox couple). The order of magnitude of the discrepancy is usual. In the standard AgCl/Ag electrode a_{Cl^-} = 1 mol./kg, which does not exactly correspond to a 1M (or even 1m) KCl or NaCl solution: it is not clear whether the author made this difference (he does not give the exact composition of his (real) AgCl/Ag electrode): typically the normal potential of the AgCl/Ag electrode made with 1 M KCl (0.243_3 V), is nearly the same as the potential of the saturated calomel electrode. Anyhow, the composition of the solution of this AgCl/Ag electrode could not be the same as the working solutions (it is not stable when in contact with CO_3^{-2} anion) and finally the junction potential was probably not the same during the working and calibration measurements. This review assumed that all these possible systematic errors are taken into account by measured junction potential. The reproducibility on each experimental data calculated by this review (1.96 σ) is less than 8 and 32 mV in Na_2CO_3 and K_2CO_3 media respectively. No other uncertainty is added to the SIT regression results (table [77SIM]-2).

The figure given in this publication was used to get the original experimental data. The junction potential was measured (given in the table of this publication): first using linear interpolation (or extrapolation for the last point), then shifting it to obtain 0 V in 1 M K^+ solution (i.e. 0.5 M K_2CO_3) where it should be near 0. Finally these corrections give a practical potential of the reference calomel electrode of $0.266_3 + 0.021 - 0.043 = 0.244_3$ V/N.H.E in the 0.5 M K_2CO_3 solution: this value is exactly the theoretical one. In the other solutions it is shifted by the difference between the junction potentials indicated in the second column of the table [77SIM]-1.

The extrapolations to zero ionic strength (figure [77SIM]-2, Table [77SIM]-2) fit surprisingly well for all the data of this [77SIM] publication in both Na^+ and K^+ media. Δε values are not the same in Na^+ and K^+ media. This difference is probably due to special ionic strength effect (typically ion pairing) with the highly charged complex(es). The same idea has already been proposed to explain unusual values of ε coefficients for this type of species [89RIG, 92GRE/FUG] and to explain differences between uranium and transuranians [92CAP, 95OFF/CAP] (Table [77SIM]-2). Still the ε numerical

Table [77SIM]-2: SIT regression for the redox potential of the Np(VI)/Np(V) couple measured in Na_2CO_3 and K_2CO_3 aqueous solutions. The experimental data used for SIT regression are from the table [77SIM]-1 or from the first reference indicated in the last column. ± is 1.96σ. This [77SIM] publication and the [95OFF/CAP] one are the only reliable work published. For comparison U and Pu Δε data are tabulated. For U, Δε vary with the ionic strength, in contradiction with one of the SIT hypothesis, this was attributed to U(V)-Na^+ ion pairing [89RIG, 92GRE/FUG].

Δε	±	E°/A	±	E°	±	Medium	Reference
0.07_3	0.13_8	5.72_0	0.35_5	0.338	0.021	Na_2CO_3	[75SIM, 77SIM] calculated by this review
0.08_1	0.02_5	5.89_8	0.05_3	0.349	0.003	Na_2CO_3	[77SIM] calculated by this review
0.15	0.05			0.341	0.017	Na_2CO_3	[95OFF/CAP]
0.92	0.10					$NaClO_4$ (Na_2CO_3)	U [89RIG, 92GRE/FUG]
0.91	0.02					$NaClO_4$ (Na_2CO_3)	U [92CAP]
0.63	0.11					$NaClO_4$ (Na_2CO_3)	U [92CAP] calculated from the data at I ≤ 2 M
0.18	0.02					Na_2CO_3	Pu [92CAP]
-0.07_9	0.04_8	5.77_5	0.16_4	0.342	0.010	K_2CO_3	[74SIM/VOL, 77SIM] calculated by this review
-0.04_7	0.05_1	5.75_6	0.19_8	0.341	0.012	K_2CO_3	[77SIM] calculated by this review

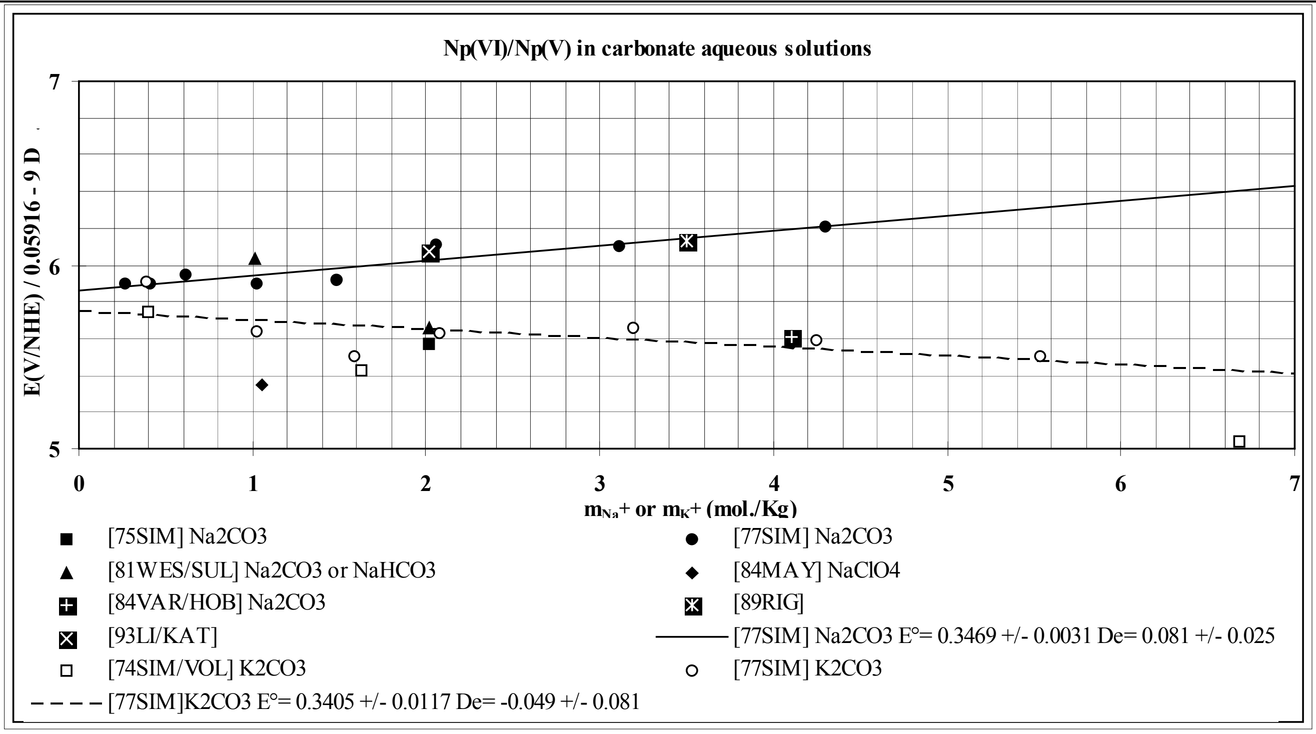


Figure [77SIM]: Redox potential of the Np(VI)/Np(V) couple measured by Simakin in Na_2CO_3 and K_2CO_3 aqueous solutions [77SIM] (table [77SIM]-1 and 2.) and previous works. The uncertainties written on the figure are deduced from statistical analysis, it must be increased for possible systematic error as discussed in the text. The lines are plotted with the values indicated on the figure. These values are the results of (unweighted) SIT regressions (using all the data shown on this figure). These [77SIM] data are used together with [95OFF/CAP] later work to calculate the values proposed in this review (see the corresponding chapter).

values are here quite reasonable. SIT regression (figure [77SIM]-2, Table [77SIM]-2) results are also in good agreement with later work [95OFF/CAP] in Na_2CO_3 media (Table [77SIM]-2).

These results are consistent with previous data [74SIM/VOL, 75SIM] (figure [77SIM]): they were all published by the same author; but for this previous work there is not any information on junction potential, and the potential was measured versus another reference electrode. For these reasons the previously published potential data were not shifted for systematic error correction (and were not used by this review to select thermodynamic data).

[78BAS/FER]

Basile L.J., Ferraro J.R., Mitchell M.L., Sullivan J.C. *The Raman Scattering of Actinide (VI) ions in Carbonate Media*. Applied Spectro., 32, 6 (1978) 535-537.

There is not any thermodynamic data in this work.

[81WES/SUL]

Wester, D.W., Sullivan, J.C. *Electrochemical and spectroscopic studies of neptunium(VI), -(V), and -(IV) in carbonate-bicarbonate buffers*, Inorg. Nucl Chem, 43,11 (1981) 2919-2923.

The redox potential of the Np(VI)/Np(V) couple is measured in 1 M Na_2CO_3 and 1 M $NaHCO_3$ solutions. The authors say that their measurements, 0.221 V/S.C.E is in very good agreement with [74SIM/VOL, 77SIM] previous works, which is approximately the case (figure [95OFF/CAP]-6).

[83MAD/HOB]

Madic, C., Hobart, D.E., Begun, G.M. *Raman spectrometric studies of actinide(V) and -(VI) complexes in aqueous sodium carbonate solution and of solid sodium actinide(V) carbonate compounds*, Inorg. Chem., 22 (1983) 1494-1503.

No data from this publication are used in the present review.

[84MAY]

Maya, L. *Carbonate complexation of dioxoneptunium(VI) at 25 C: its effects on the Np(V)/Np(VI) potential*, Inorg. Chem., 23 (1984) 3926-3930.

The aim of this work was to determine the Np(VI) speciation in bicarbonate and carbonate aqueous solutions, by using potentiometric and electrochemical techniques. The author pointed out, that the formation constants he calculated from his titration experimental data, poorly model his experimental electrochemical data. For the carbonic acid equilibria, the author did not use exactly the same constants as in the present review (table [84MAY]-3).

Measurements of the potential of the Np(VI)/Np(V) couple

The author had some experimental difficulties (precipitation, non reversibility or reproducibility on solid electrode) to measure the potential of the Np(VI)/Np(V) redox couple. He used a saturated calomel reference electrode; but he did not mention that he took into account the junction potential, for this reason this review added 30 mV to the E'° uncertainty. The potential measured in the most concentrated [CO_3^{2-}] solution is constant, and its numerical value, is consistent with the observation of several other authors only if the uncertainty is increased. This potential increases with $\log_{10}P_{CO_2}$ by (0.114 ± 0.019), (0.110 ± 0.012) and (0.095 ± 0.016) mV/$\log_{10}P_{CO_2}$ unit at respectively 55, 27 and 14 mM of total alkalinity (figure [84MAY]-3). This corresponds to 1.93 ± 0.16, 1.85 ± 0.21 and 1.60 ± 0.28 CO_2 exchanged with each electron. The same type of slope analysis versus the alkalinity suggests to interpret these data with the following equilibria in bicarbonate media (where [HCO_3^-] ≈ alkalinity is constant in a wide domain for each set of experiments):

$$NpO_2(CO_3)_3^{4-} + e^- + i\ CO_2 + i\ H_2O \Leftrightarrow NpO_2(CO_3)_{3-i}^{2i-5} + 2\ i\ HCO_3^-$$

where i is among 1 and 2 (nearly 2). This is consistent with Np(VI) and Np(V) chemistry: the complexes of Np(VI) are more stable than those of Np(V) (this experimental observation is usually attributed to the fact that the NpO_2^{2+} cation has a higher charge than the NpO_2^+ one); the Np(V) limiting complex, $NpO_2(CO_3)_3^{5-}$, should then dissociate before the Np(VI) one. It is much simpler to write the above equilibrium with only CO_3^{2-} since, according to this interpretation, only this cation is exchanged (in the chemical domain where the above slope values were observed). For this reason, Maya's data are plotted as a function of $\log_{10}[CO_3^{2-}]$ (figure [84MAY]-1) where it appears that all the experimental points nearly fall on a single line: the points at the highest [CO_3^{-2}] are above this line by a few to 20 mV. This small systematic deviation can be attributed to some experimental error (typically checking of the reference electrode from one set of measurements to another one) or to the formation of minor Np(VI) hydroxide complex. Nevertheless, this review interpreted the data with the following equilibria

$$NpO_2(CO_3)_{3-i}^{2i-4} + e^- \Leftrightarrow NpO_2(CO_3)_{3-j}^{2j-5} + (j - i)\ CO_3^{-2}$$

This does not take into account all the possible (pure carbonate) complexes since the formation of $(NpO_2)_3(CO_3)_6^{6-}$ is well established [86GRE/RIG, 89RIG]. It seems (this is not clear in the publication) that the redox measurements were performed at very low Np concentration: neglecting this polynuclear species should then induce only a small systematic error.

$\beta_{a,b,x}$ is the notation used in [84MAY], for the equilibria

$$a\ NpO_2^{2+} + b\ CO_2 + (b + x)\ H_2O \Leftrightarrow (NpO_2)_a(CO_3)_b(OH)_x^{2\,a\,-\,2\,b\,-\,x} + (2\ b + x)\ H^+$$

$$\beta_{a,b,x} = \frac{\left[a,b,x\right]\left[H^+\right]^{2\,b+x}}{\left[NpO_2^{+2}\right]^a P_{CO_2}^b}$$

Here a,b,x is a notation for $(NpO_2)_a(CO_3)_b(OH)_x^{2\,a\,-\,2\,b\,-\,x}$. $\beta'_{a,b,x} = \beta_{a,b,x} / \beta^{a'}_{a°,b°,x°}$ are the constant of the

$$a'\ (NpO_2)_{a°}(CO_3)_{b°}(OH)_{x°}^{2\,a°\,-\,2\,b°\,-\,x°} + b'\ CO_2 + (b' + x')\ H_2O \Leftrightarrow (NpO_2)_a(CO_3)_b(OH)_x^{2\,a\,-\,2\,b\,-\,x} + (2\ b' + x')\ H^+$$

equilibria studied in this work, with the same definitions as below (for the interpretation of the potentiometric data).

Doing so it is obvious (table [84MAY]-2) that, in contradiction with the discussion of the author, the only equilibrium constant directly measured by both techniques, $\beta'_{1,2,0} = \beta_{1,2,0} / \beta_{1,3,0}$ or the corresponding β_2 / β_3, of the

$$NpO_2(CO_3)_3^{-4} \Leftrightarrow NpO_2(CO_3)_2^{-2} + CO_3^{-2}$$

equilibrium is in fact consistent. Only the addition of the $NpO_2(CO_3)_2^{-2}$ soluble Np(VI) complex possibly improves the curve fitting results (table [84MAY]-2). Even without any fitted formation constant (the complexing constants of Np(V) are fixed, taken from [83MAY] previous work of the same author in the same conditions, they are consistent with those selected in the present review), the model can reasonably predict the experimental data. Hence the main explanation of the shape of the curve representing the variations of the redox potential, is the dissociation of the Np(V) limiting complex, $NpO_2(CO_3)_3^{-5}$, into $NpO_2(CO_3)_2^{-3}$, $NpO_2CO_3^-$ and NpO_2^+. The constants of the corresponding equilibria were not re-fitted here. The dissociation equilibria of the carbonate limiting complex of Np(VI), $NpO_2(CO_3)_3^{-4}$, does not really affect the curve fitting. One should not rely on the result of this curve fitting for this reason and for the following possible systematic errors:

Table [84MAY]-1 Potential of the Np(VI)/Np(V) redox couple measured in bicarbonate/carbonate media. I = 1 M ($NaClO_4$), T = 25°C. The experimental data were scanned from the figure 5 of the [84MAY] reference.

$\log_{10}P_{CO_2}$ ($\log_{10}$atm)	alkalinity (M)	E V/N.H.E	alkalinity (M)	E V/N.H.E	alkalinity (M)	E V/N.H.E	alkalinity (M)	E V/N.H.E
-5.5	0.2	0.435	0.005	0.552	0.0027	0.59	0.0014	0.625
-2.45			0.005	0.69	0.0027	0.775	0.0014	0.855
-2	0.2	0.45	0.005	0.75	0.0027	0.83	0.0014	0.905
-1.45	0.2	0.48	0.005	0.805	0.0027	0.885	0.0014	0.95
0	0.2	0.608						

Table [84MAY]-2 Formation constants of Np(VI) carbonate complexes obtained from curve fitting of the Np(VI)/Np(V) redox data in bicarbonate/carbonate media. $K_i = [NpO_2(CO_3)_i^{2-2i}] [CO_3^{2-}]^{3-i} / [NpO_2(CO_3)_3^{-4}] = \beta_i^{VI} / \beta_3^{VI}$. The experimental data are from the table [84MAY]-1 (I = 1 M $NaClO_4$, T = 25°C). This review used (without fitting them) complexing constant of Np(V) in these conditions measured by the same author [83MAY] (they are consistent with the value selected in this review): $\log_{10}\beta_1^V = 4.49$, $\log_{10}\beta_2^V = 7.11$ and $\log_{10}\beta_3^V = 8.53$. The total concentration of Neptunium seems to have been 2 µM. Σ is the least square sum. The interpretation (of this publication) proposed by this review is bolded.

Σ	E°	±	$\log_{10} K_2$	±	$\log_{10} K_1$	±	$\log_{10} K_0$	±	calculated by:
0.123	0.425	0.086							this review
0.123	$0.426^{(1)}$	0.084							this review
0.054	0.446	0.037	-4.74	1.00					this review
0.079	$0.426^{(1)}$	0.045	-5.19	1.52					this review
			-4.51						[84MAY] redox
			-4.64	0.09					[84MAY] pot
0.053	0.445	0.036	-4.88	1.07	-11.14	1.81			this review
0.075	$0.426^{(1)}$	0.044	-5.72	1.96	-11.13	1.97			this review
0.053	0.445	0.036	-4.85	1.05	-11.47	2.14	-17.66	2.52	this review
0.075	**$0.426^{(1)}$**	**0.044**	**-5.72**	**1.96**	**-11.14**	**1.97**	-19.23	4.36	this review
0.075	$0.426^{(1)}$		-5.72		-11.13		-20.00		this review(2)
							-20.17	**0.37**	this review(3)
			-6.23	0.15	-13.46	0.10	-21.91	0.07	U(VI) [92GRE/FUG]

(1) E° = 0.4263 is fixed to account for the points at the highest $[CO_3^{2-}]$ (see the text and the figure [84MAY]-1).

(2)The following values of the formation constant of monomer hydroxide complexes are fixed: $\log_{10}{}^*\beta_1 = -5.17$ and $\log_{10}{}^*\beta_3 = -19.18$, taken respectively from [72CAS/MAR] and (for Uranium) [92GRE/FUG].

(3)β_3 is calculated from the potential shift for the Np(VI)/Np(V) redox potential between non complexing and concentrated carbonate media (see the text). The $-\log_{10}\beta_3 = \log_{10}K_0$ value selected by this review from [77SIM, 89RIG, 95OFF/CAP] more reliable works, is -20.17 ± 0.37.

Table [84MAY]-3 Equilibrium constants of the carbonic acid equilibria in $NaClO_4$ aqueous solutions used in [84MAY]. $Kp_1 = P_{CO_2} /([HCO_3^-] [H^+])$, $K_1 = [HCO_3^-] /([CO_3^{2-}] [H^+])$ and $Kp_2 = Kp_1 K_1$. The values of the specific interaction coefficients, ε, of the carbonates ions were re-adjusted during the present series of review (see the corrections of [92GRE/FUG] in [95SIL/BID] pages 349-351) to get equilibrium constant values of the same accuracy as the original experimental data, when using the SIT to calculate them. Still, since the ε numerical values are tabulated with 2 digits, the second digit of equilibrium constant cannot exactly fit the experimental values in typically 1 M media as in [84MAY]. This (small) problem cannot then explain the (quite small anyhow) difference with the values used in [84MAY]. When using external values of equilibria involving CO_3^{2-} or when converting $\beta_{a,b,x}$ to the usual carbonate equilibrium constants $\log_{10}K_{a,b,x} = \log_{10}\beta_{a,b,x} + b \log_{10}Kp_2$, the values of the present review were used increasing the uncertainty ($\log_{10}Kp_2 = 17.21 \pm 0.10$).

I (M)	$\log_{10} Kp_1$	±	$\log_{10} K_1$	±	$\log_{10} Kp_2$	±	Reference
0	7.82	0.04	10.33	0.02	18.15	0.04	This review
1	7.61	0.05	9.59	0.05	17.21	0.06	This review
1	7.56		9.55		17.11		[84MAY]
3	7.994	0.094	9.605	0.125	17.600	0.155	This review

First, as already mentioned; the total Np(VI) concentration is not known, it is then not possible to check whether polynuclear complexes (typically $(NpO_2)_2CO_3(OH)_3^-$ as described in the other part of this publication) were one of the minor species

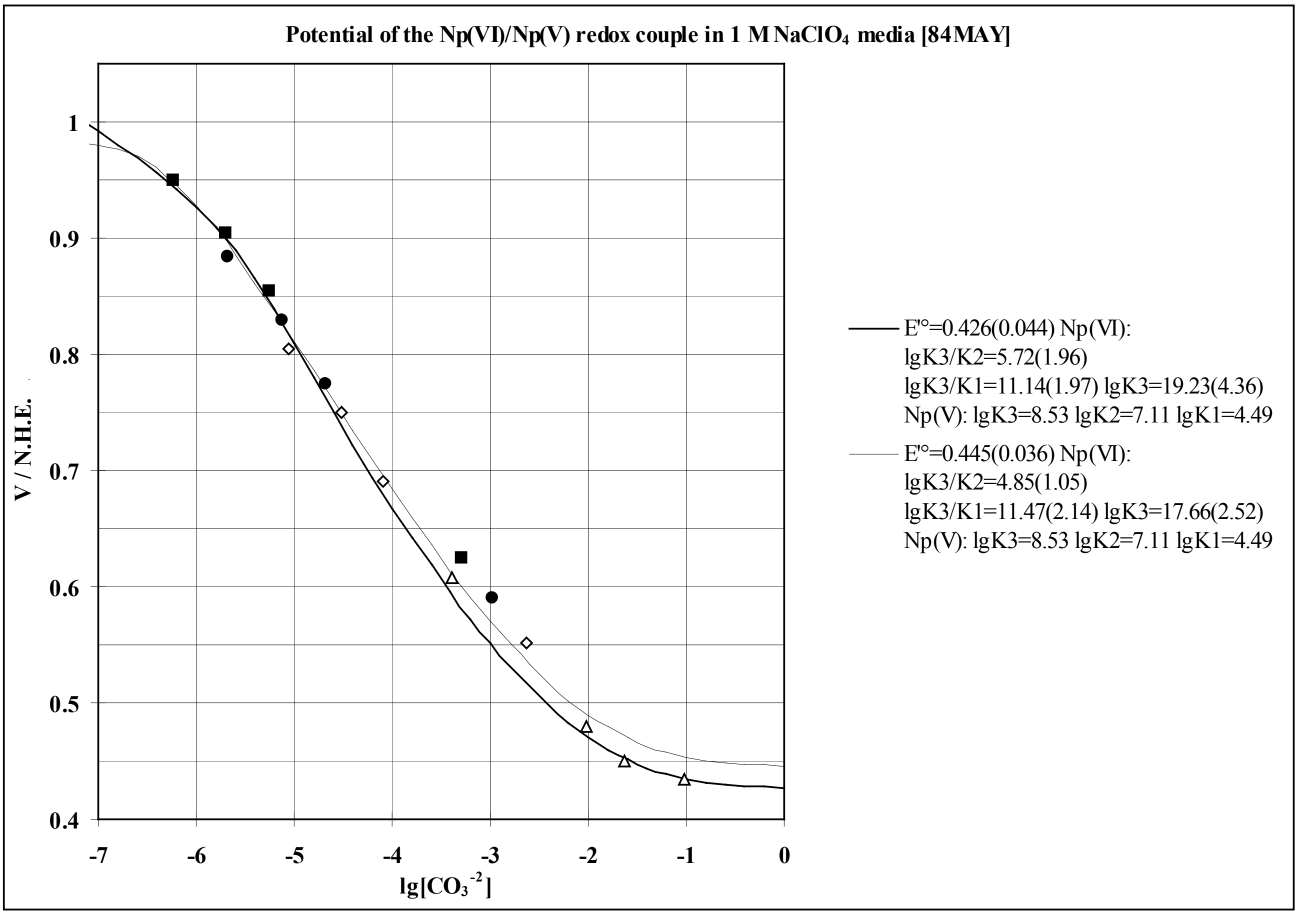


Figure [84MAY]-1: Measurements of the potential of the Np(VI)/Np(V) redox couple. Total alkalinity is ([84MAY]-1): 1.4(■), 2.7(•), 5.5(◊) or 200(Δ) mM. The lines were drawn with the values (table [84MAY]-2) indicated on the figure, where $Ki = [NpO_2(CO_3)_i^{(1or2)-2i}]\ [CO_3^{-2}]^{3-i} / [NpO_2(CO_3)_3^{-4}]$. Values in parenthesis are the statistical error (1.96 σ). The reinterpretation by this review is the thick line (where E° = 0.426 is fixed); the "best fit" is the thin one. No polynuclear species could be taken into account since the author did not indicate the total metal concentration; it seems that it was 2 μM, the influence of polymeric species should then be quite low.

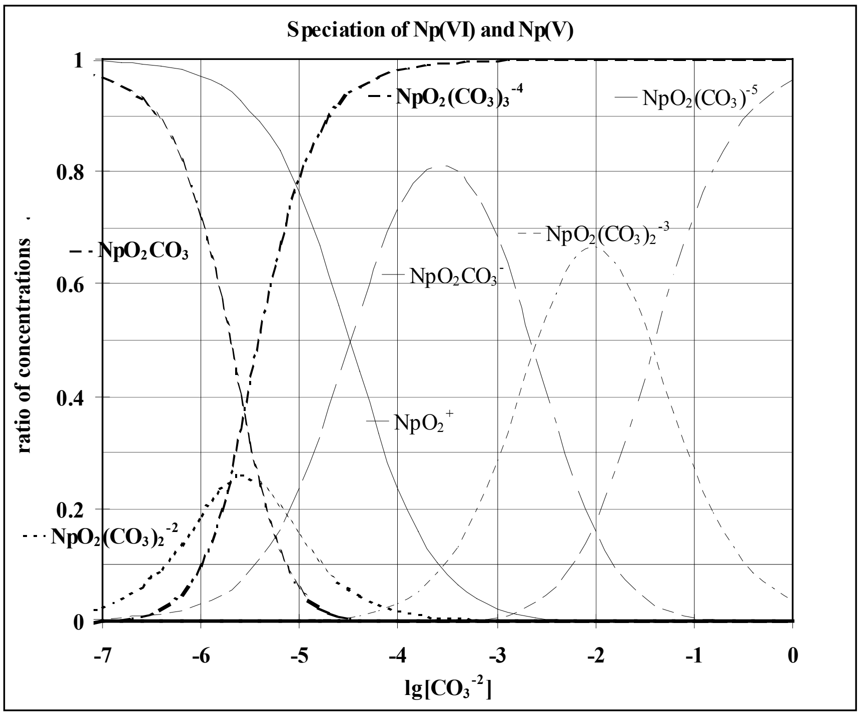


Figure [84MAY]-2: Calculated speciation of Np(VI) and Np(V) corresponding to the figure [84MAY]-1. $[NpO_2(CO_3)_n^{1-2n}] / [Np(V)]_{total}$ (thin lines) and $[NpO_2(CO_3)_n^{2-2n}] / [Np(VI)]_{total}$ (tick lines) are plotted.

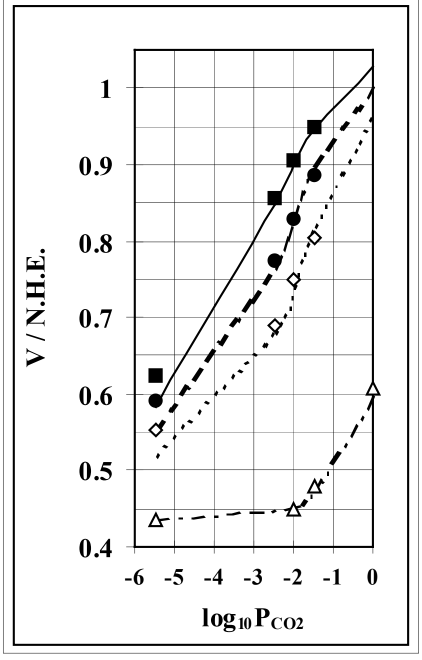


Figure [84MAY]-3: Np(VI)/Np(V) redox couple potential as plotted in [84MAY], it is the same data and curves as in the figure [84MAY-1]: total alkalinity is 0.0014 (■), 0.00027 (•), 0.0055 (◊) and 0.2 M (Δ)

Second, even if the polynuclear complexes can be disregarded, besides the pure carbonate ones (namely $NpO_2(CO_3)_2^{-2}$ and $NpO_2CO_{3(aq)}$) and NpO_2^{+2}, several poorly known monomeric Np(VI) complex could be formed; typically pure hydroxide Np(VI) complexes could also be formed namely $NpO_2(OH)_3^-$ (the corresponding complex is proposed for Uranium [92GRE/FUG]) and possibly $NpO_2(OH)_{2(aq)}$. Only the formation constant of NpO_2OH^- is known. Anyhow the addition of fixed (reasonable) values of the corresponding hydroxide equilibrium constants, did not change much the curve fitting results (table [84MAY-2]).

The best fit (figure [84MAY]-1) shows a systematic error at high carbonate concentration. This is a classical fitting artefact due to the smaller number of experimental data in these experimental conditions, since the fitting does not make any difference between scattering of the points and systematic deviations. While the other constants are fitted, the (constant) normal potential of the

$$NpO_2(CO_3)_3^{-4} + e^- \Leftrightarrow NpO_2(CO_3)_3^{-5}$$

equilibrium was then fixed at $E'^{\circ}_{NpO_2(CO_3)_3^{-4}/NpO_2(CO_3)_3^{-5}} = 0.426_3 \pm 0.044$ V/N.H.E
to obtain a better fit at high $[CO_3^{-2}]$ (figure [84MAY]-1), instead of the fitted value 0.445±0.036 V/N.H.E (table [84MAY]-2). These values agree (within the big uncertainty) with the following reliable ones:
$E'^{\circ}_{NpO_2(CO_3)_3^{-4}/NpO_2(CO_3)_3^{-5}} = 0.464_9 \pm 0.003_6$ V/N.H.E calculated from [77SIM]
and $E'^{\circ}_{NpO_2(CO_3)_3^{-4}/NpO_2(CO_3)_3^{-5}} = 0.459_6 \pm 0.007_1$ V/N.H.E calculated from [95OFF/CAP]
The value of the formation constant of the Np(VI) limiting complex, β_3^{VI}, is obtained from the shift between the Np(VI)/Np(V) potential measured here ($E'^{\circ}_{NpO_2(CO_3)_3^{-4}/NpO_2(CO_3)_3^{-5}}$) and its value in 1 M $HClO_4$ ($E'^{\circ}_{NpO_2^{+2}/NpO_2^{+}}$ = 1.140 ± 0.007 V/N.H.E. SELECTED IN THIS REVIEW?):
$\log_{10}(\beta_3^{VI}/\beta_3^{V}$ in 1 M $NaClO_4)$ = 12.06 ± 0.75 for $NpO_2(CO_3)_3^{4-} + NpO_2^+ \Leftrightarrow NpO_2(CO_3)_3^{-5} + NpO_2^{+2}$
to compared with $11.62_5 \pm 0.09_7$ calculated from [77SIM]
$11.53_5 \pm 0.14_3$ calculated from [95OFF/CAP]
and finally using as above $\log_{10} \beta_3^V = 8.54 \pm 0.3$ [83MAY]
$\log_{10}(\beta_3^{VI}$ in 1 M $NaClO_4)$ = 20.59 ± 0.76 for $3\ CO_3^{-2} + NpO_2^{+2} \Leftrightarrow NpO_2(CO_3)_3^{-4}$
$20.02_3 \pm 0.35_4$ calculated from [77SIM]
$20.11_3 \pm 0.37_3$ calculated from [95OFF/CAP]
(for Uranium 21.91 ± 0.07 calculated from [92GRE/FUG])

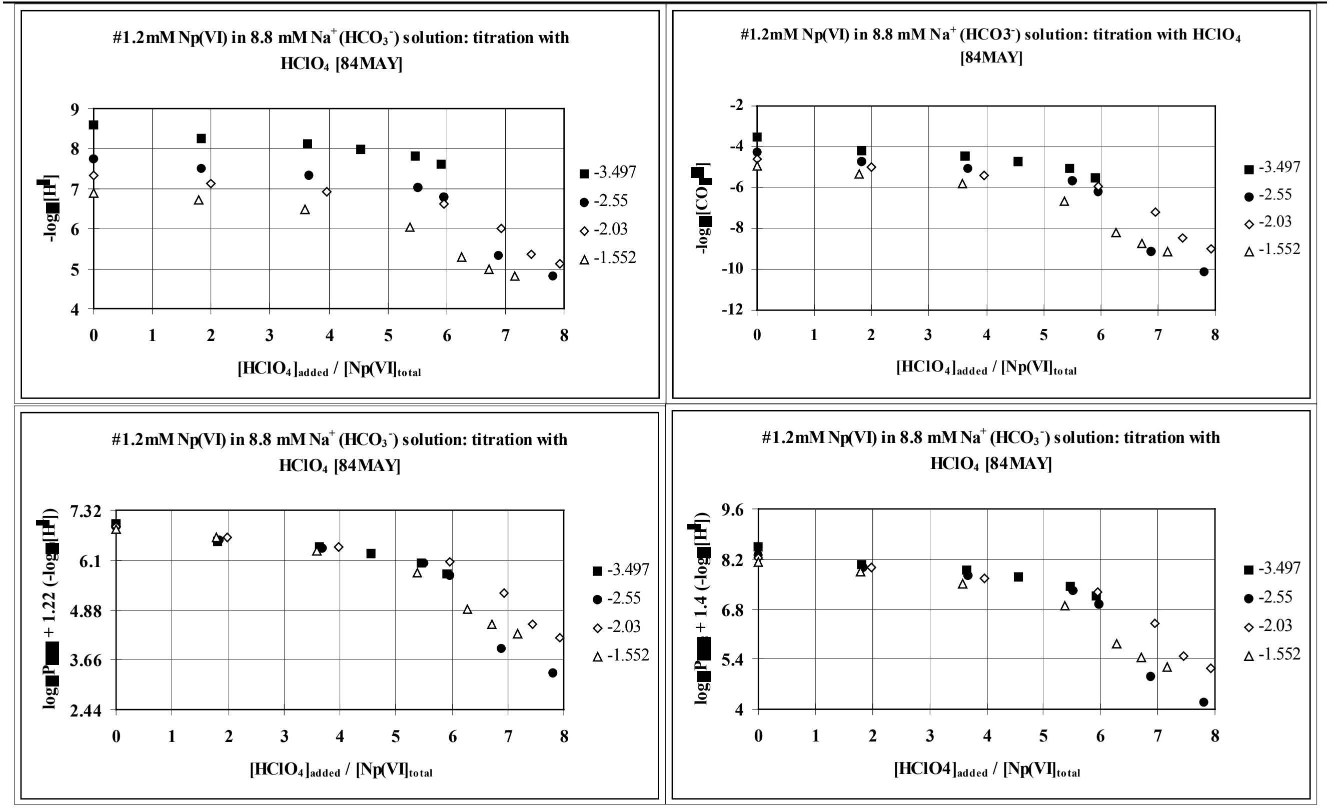
When fixing the $E'^{\circ}_{NpO_2(CO_3)_3^{-4}/NpO_2(CO_3)_3^{-5}}$ value instead of fitting it, the most important change is not on the $E'^{\circ}_{NpO_2(CO_3)_3^{-4}/NpO_2(CO_3)_3^{-5}}$ value itself, but on the first dissociation constant of the limiting complex: $\log_{10}K_2 = -4.8_5 \pm 1.0_5$ is changed to $-5.7_2 \pm 1.9_6$ (table [84MAY]-2). The curve fitting results (figure [84MAY]-1 and table [84MAY]-2) are
$\log_{10}(\beta_2/\beta_3$ in 1 M $NaClO_4)$ ≤ -5.72 ± 1.96 for $NpO_2(CO_3)_3^{4-} \Leftrightarrow NpO_2(CO_3)_2^{-2} + CO_3^{2-}$
(-6.23 ± 0.15 for U calculated from [92GRE/FUG])
$\log_{10}(\beta_1/\beta_3$ in 1 M $NaClO_4)$ ≤ -11.14 ± 1.97 for $NpO_2(CO_3)_3^{4-} \Leftrightarrow NpO_2CO_3^0 + 2\ CO_3^{2-}$
(-13.46 ± 0.10 for U calculated from [92GRE/FUG])
$-\log_{10}(\beta_3$ in 1 M $NaClO_4)$ ≤ -19.23 ± 4.36 for $NpO_2(CO_3)_3^{4-} \Leftrightarrow NpO_2^{2+} + 3\ CO_3^{2-}$
(-21.91 ± 0.07 for U calculated from [92GRE/FUG])
This last value ($\log_{10}\beta_3 = 19.23 \pm 4.36$) is consistent with the value (20.59±0.76) deduced below from the series of β_i/β_3 values calculated above; but it is more accurate. Inequality indicates that this review considers the results of this reinterpretation as maximum possible values; still, since the above species are stable for obvious chemical reasons, and since the uncertainty estimates are large enough (there are not deduced from their own standard deviation but they are the values that induce an increase by 1.96 Σ of the overall least square sum, Σ) the actual values are probably within the uncertainty proposed here. Using $\log_{10}\beta_3 = 20.59 \pm 0.76$ and the above series of β_i/β_3 values (for i = 1 and 2) one obtains
$\log_{10}(\beta_2$ in 1 M $NaClO_4)$ ≤ 14.87 ± 2.10
(15.67 ± 0.13 for Uranium calculated from [92GRE/FUG])
$\log_{10}(\beta_1$ in 1 M $NaClO_4)$ ≤ 9.46 ± 2.11
(8.44 ± 0.07 for Uranium calculated from [92GRE/FUG])
which again are more accurate values than the ones calculated only from the series of the β_i/β_3 values (13.51 ± 4.78 and 8.09 ± 4.78 respectively).

The β_i values estimated here for Np(VI) are of the same order of magnitude than those of Uranium calculated from the data selected in [92GRE/FUG]. β_3 is a bit smaller for Np(VI) than for U(VI): this type of (here very small) difference is usually attributed to the diminution of the ionic radius from U to Np, that is expected to enhance the steric repulsion between the ligands of the limiting complex. The diminution of the ionic radius should, in opposition stabilise the ligand-cation (rather ionic) bound in the complex of the smallest cation (i.e. Np). but ionic strength effect could decrease this variation. Anyhow the measurements of β_1 and β_2 are not accurate enough to see a difference between U and Np. As already mentioned, the values of β_i/β_3 calculated here (and hence the β_i values deduced from them) are only estimations (this is reflected by the uncertainties).

For comparison the stepwise constants are
$\log_{10}(\beta_2/\beta_1$ in 1 M $NaClO_4)$ ≈ 5.41 ± 2.98
(7.23 ± 0.15 for Uranium calculated from [92GRE/FUG])
$\log_{10}(\beta_3/\beta_2$ in 1 M $NaClO_4)$ ≥ 5.72 ± 1.96
(6.23 ± 0.15 for Uranium calculated from [92GRE/FUG]))
Accordingly, the Uranium dicarbonato complex, $UO_2(CO_3)_2^{2-}$, predominates over 1.00±0.21 $\log_{10}[CO_3^{-2}]$ unit. The corresponding neptunium complex, $NpO_2(CO_3)_2^{2-}$, might have a smaller predominating domain: the limiting complex,

Table [84MAY]-4 Experimental data of potentiometric titration of Np(VI) used in the present review, they are taken or calculated from the reference [84MAY]. eq is $[HClO_4]_{added}$ / $[Np(VI)]_{total}$.

eq	lg P_{CO_2}	$\log_{10}[Np]_t$	$-\log_{10}[H^+]$	eq	lg P_{CO_2}	$\log_{10}[Np]_t$	$-\log_{10}[H^+]$
0	-3.497	-2.914	8.585	0	-2.03	-2.951	7.333
1.821	-3.497	-2.923	8.237	1.984	-2.03	-2.960	7.129
3.643	-3.497	-2.933	8.124	3.968	-2.03	-2.970	6.924
4.554	-3.497	-2.937	7.983	5.952	-2.03	-2.979	6.636
5.464	-3.497	-2.942	7.805	6.944	-2.03	-2.983	6.010
5.920	-3.497	-2.944	7.601	7.440	-2.03	-2.986	5.376
				7.937	-2.03	-2.988	5.117
0	-2.55	-2.917	7.751	0	-1.552	-2.907	6.902
1.837	-2.55	-2.927	7.496	1.792	-1.552	-2.916	6.716
3.673	-2.55	-2.936	7.332	3.584	-1.552	-2.925	6.469
5.510	-2.55	-2.945	7.036	5.376	-1.552	-2.935	6.030
5.969	-2.55	-2.947	6.783	6.272	-1.552	-2.939	5.283
6.887	-2.55	-2.952	5.325	6.720	-1.552	-2.941	5.000
7.805	-2.55	-2.956	4.826	7.168	-1.552	-2.944	4.802



Figures [84MAY]-5 Potentiometric titration of Np(VI) at different carbonic gas partial pressure. The numbers on the figures are $\log_{10}(P_{CO_2}(atm))$. The same data (table [84MAY]-4) are plotted in each figure; but instead of *pH* (or rather $-\log_{10}[H^+]$), $-\log_{10}[H^+] + x \log_{10}P_{CO_2}$ or $\log_{10}[CO_3^{-2}]$ is plotted as a function of the equivalent acidity added. If the starting species, $NpO_2(CO_3)_3^{4-}$, is dissociated into only carbonate complexes ($NpO_2(CO_3)_2^{2-}$ or $(NpO_2)_2(CO_3)_6^{-6}$ typically) the $\log_{10}[CO_3^{-2}]$ plot should fall on a single curve (which is not the case). If the major dissociated complex is $(NpO_2)_2CO_3(OH)_3^-$, $(NpO_2)_3(OH)_7^-$ or $(NpO_2)_3(OH)_8^{-2}$ the $-\log_{10}[H^+] + x \log_{10}P_{CO_2}$ plot should fall on a single curve for x = 1.4, 1.22 and 1.11 respectively which could be the case (bottom figures) in the buffering region before the corresponding equivalent points at 3.5, 3.67 and 3.33 equivalents of H^+ added. These are then possible interpretations; but other qualitative criteria must also be fulfilled (figure [84MAY]-6 and table [84MAY]-5).

$NpO_2(CO_3)_3^{4-}$, might dissociate nearly directly into NpO_2CO_3 this possibility was ignored by Maya, when he interpreted his potentiometric data (in the same [84MAY] publication), which are now discussed.

Potentiometric titration of Np(VI) from carbonate media

$HClO_4$ solution was added to a Np(VI) carbonate solution where P_{CO_2} was maintained constant by bubbling through the working solution, carbonic gas preequilibrated with an aqueous solution of the same ionic strength. Ionic strength was constant (1 M $NaClO_4$). $-\log_{10}[H^+]$ was measured with a glass electrode that had been calibrated in concentration. The author tried different models (set of complexes) to interpret his potentiometric data and gave the corresponding curve fitting results, where he also used the known formation constants of some pure hydroxide complexes [72CAS/MAR] as fixed parameters. All this is correct methodology. He concluded that the limiting complex of Np(VI) was dissociated (besides the [72CAS/MAR] known pure hydroxide ones) into the $NpO_2(CO_3)_2^{-2}$ and $(NpO_2)_2CO_3(OH)_3^-$ for which he fitted the formation constants; but, as mentioned by the author, the curve fitting results themselves, are not enough to draw a unique conclusion (to propose a unique model or interpretation): he then had to use independent qualitative chemical information to finally choose his interpretation. Unfortunately it is not demonstrated that he chose the best one (or the right one) for the following reasons

First the statistical interpretation is not really correct for several reasons.

- The values of some fitted parameters are correlated and this is a classical feature when some experimental parameters are not varied enough (namely here a unique total Np(VI) concentration was used for all the measurements, and a to narrow domain of CO_2 partial pressure was used as explain below).
- Different models did not give a clear difference in the overall least square sum, Σ, typically it was not clear (considering only the statistical results) whether $(NpO_2)_3(OH)_7^-$ or / and $(NpO_2)_3(CO_3)_6^{-6}$ or / and possibly $(NpO_2)_3(OH)_8^{-2}$ (table [84MAY]-5), should be added or not to the model (the corresponding Uranium complexes are stable).

Second, as observed by the author, the overall formation constants deduced from these potentiometric data do not agree with those deduced from the electrochemical data. As already mentioned the values of only one stepwise constant is consistent when comparing both determinations (table [84MAY]-2).

Third there are several chemical details that could accumulate approximations or even small systematic errors.

- According to the interpretation of the author (figure [84MAY]-7), the final product of the titration is NpO_2^{2+}: he then assumed that $NpO_2(CO_3)_2^{-2}$ is one of $NpO_2(CO_3)_3^{-4}$ main dissociated product, but surprisingly not $NpO_2CO_{3(aq)}$ which is the intermediary species between the (assumed) first dissociated one, $NpO_2(CO_3)_2^{-2}$, and the final species, NpO_2^{+2} (figure [84MAY]-10).
- In addition, the above reinterpretation of the electrochemical data, and Uranium behaviour indicated that $NpO_2CO_{3(aq)}$ is probably stable in a broader domain than $NpO_2(CO_3)_2^{-2}$.
- The author [84MAY] excluded the $(NpO_2)_3(CO_3)_6^{-6}$ species. This does not seem to be much consistent with his own fitting results (table [84MAY]-5, fit 5 typically). Unfortunately the stability of this ($(NpO_2)_3(CO_3)_6^{-6}$) species is now well established [86GRE/RIG, 89RIG]; and the absorption spectrum of this ($(NpO_2)_3(CO_3)_6^{-6}$) species was clearly detected later [86GRE/RIG, 89RIG] in nearly the same chemical conditions as Maya's measurements [84MAY]. This contradiction was already pointed out in [86GRE/RIG]. The author [84MAY] excluded this species because he obtained worst fitting results (table [84MAY]-5, fit 4); but this species could as well be included in nearly the best fit (table [84MAY]-5, fit 5).
- The author should also have used the highest possible CO_2 partial pressure to obtain a simpler chemical system with probably only pure carbonate complexes (figure [84MAY]-11), and only then he should have used lower partial pressure where the competition with the OH^- ligand induces the formation of new (mixed polymeric) species.
- It was also observed later [86GRE/RIG, 89RIG] that, in contradiction with the chemical behaviour of its two neighbours in the Mendeleev's periodic table, U(VI) and Pu(VI), the precipitation of $NpO_2CO_{3(s)}$ is quite slow: it lasts at least one hour for Np(VI), with apparition of a green-red original colour, possibly due to light diffusion by colloids. Then equilibrium achievement must be carefully checked: nothing was said on this subject by the author, who might have met this kinetic problem in some of his measurements, without noticing it. This kinetic problem is expected after the dissociation of the limiting carbonate complex into an unknown polymeric one (possibly $(NpO_2)_3(CO_3)_6^{-6}$ or $(NpO_2)_2CO_3(OH)_3^-$) since polymeric complexes often dissociate slowly (probably due to the kinetic stability of bridging ligands): it is then expected at the end of the titration, just before the formation of the final product, NpO_2^{2+}. This review calculated from recent solubility study [97VIT/CAP], that most Maya's measurements were certainly in oversaturated solutions (Figure [95MOR/PRA]-2). This is probably enough to induce quite large systematic deviation in the interpretation of the data; but this cannot be checked since neither filtration, neither back titration, nor spectrophotometric observation was reported (see [89RIG] who reported this type of information for measurements in similar conditions).
- There are quite few experimental data in these chemical conditions (at the equivalent point) where the wide range of pH conditions induces the formation of a bigger number of complexes (when comparing to the buffering region, i.e. before the equivalent point).
- There are obviously typing errors in some formula and numerical data that this review has corrected; but one cannot be sure that all these errors were found.
- Specially the titration curves drawn with the experimental data tabulated in the [84MAY] publication, cross each other about or just after the equivalent point (figures (84MAY]-5, 7, 9); but not on the corresponding figure of the publication.
- The author fitted the overall formation constants, $\beta_{a,b,x}$, which (as explained above) refer to the free species, NpO_2^{2+}, that is always a minor species (figures [84MAY]-8 and 10), and whose formation equilibrium might not be achieved. For this reason one should rather use $\beta'_{a,b,x} = \beta_{a,b,x} / \beta^a_{1,3,0}$, the constants of the dissociation equilibria of the limiting complex.
- The author used different carbonic gas partial pressure (and pH) which is correct to make the difference between complexes of equivalent alkalinity, but of different ratio of hydroxide to carbonate ligand, unfortunately he did not use high enough carbonic gas partial pressure as already said (see also the figures [84MAY]-11).
- There is also another key parameter that must be varied to allow the determination of the degree of polynuclearity of the intermediary complex(es): it is the total Np(VI) concentration (see also the figure [84MAY]-6). Unfortunately the author used only one of them as already noticed in [86GGRE/RIG].

Table [84MAY]-5 Species tested to interpret the potentiometric titration of Np(VI). a,b,x is an abbreviation for $(NpO_2)_a(CO_3)_b(OH)_x^{2a-2b-x}$. The slopes, s_{pHi}, of the titration curves (figure [84MAY]-5), and their shift per $\log_{10}P_{CO_2}$, s_C, were graphically measured (first columns) or calculated assuming that the starting complex, $NpO_2(CO_3)_3^{-4}$, was dissociated into only one complex, which is a rough approximation. -y'/a' is the number of equivalent acidity needed to reach the equivalent point (typically 1 equivalent CO_3^{-2} and then 2 = -y'/a' equivalent H^+ is needed to transform $NpO_2(CO_3)_3^{-4}$ into $NpO_2(CO_3)_2^{-2}$). n_i is the number of equivalent acidity at the point where s_{pHi} was measured or calculated (typically n_i = (-y'/a')/2 at the half point reaction). s_{pH1} (calculated using n_1) is the slope estimated with the two first experimental points, and s_{pH2} (using n_2) is estimated with the second and third experimental points. This slope analysis indicates the possible first major dissociated product. It is only a guide line. Slopes consistent with the experimental values are printed in bold face. The species consistent with the two slopes are printed in bold face. Tabulated $\log_{10}\beta'_{a,b,x}$ are fixed values or curve fitting results: for these last ones, the uncertainty is tabulated. $\beta'_{a,b,x} = \beta_{a,b,x} / \beta^{a}_{1,0,3}$, $\beta_{a,b,x} = [a,b,x]\,[H^+]^{2b+x}\,[NpO_2^{+2}]^{-a}\,P_{CO_2}^{-b}$. Small means that the formation constant could not be fitted. Σ'² is the sum of $([HClO_4]_{added} / [Np]_{total})$ least squares calculated by this review from the available 27 data. Σ² is $-\log_{10}[H^+]$ least square sum calculated by the [84MAY] author from 69 data. Σ_{min} is Σ minimum value. Underlined values are used by this review. The best fit proposed by the [84MAY] author, was the fit 2. Most of the data where certainly (see text) obtained in ovesaturated solutions leading to doubtful $\beta'_{a,b,x}$ values (italicised numbers)

measured			a,b,x =3,6,0	1,2,0	**3,0,8**	**2,1,3**	***3,0,7***	*1,1,0*	*3,1,3*	*3,0,5*	*1,0,1*	*2,0,2*	*1,0,0*
s_{pH1}	-0.134± 0.081		-0.281	-0.436	**-0.101**	**-0.115**	***-0.086***	***-0.152***	***-0.065***	***-0.065***	***-0.115***	***-0.068***	***-0.092***
s_{pH2}	-0.098± 0.062		0.250	0.198	-0.254	-0.196	***-0.149***	***-0.129***	***-0.077***	***-0.077***	***-0.070***	***-0.055***	***-0.048***
n_1	0.929± 0.084		2.153	2.153	3.588	3.767	*3.947*	*4.306*	*4.665*	*4.665*	*5.382*	*5.382*	*6.459*
n_2	2.788± 0.252		0.717	0.717	1.196	1.255	*1.315*	*1.435*	*1.554*	*1.554*	*1.793*	*1.793*	*2.152*
s_C	-0.841± 0.166		-0.5	-0.5	**-0.9**	**-0.714**	***-0.818***	*-0.5*	***-0.615***	***-0.692***	***-0.6***	***-0.6***	*-0.5*
fit	Σ'/Σ'$_{min}$	Σ/Σ$_{min}$	y'/a -2	-2	-3.333	-3.5	*-3.667*	*-4*	*-4.333*	*-4.333*	*-5*	*-5*	*-6*
1	1.52					41.79 ± 0.95				*72.29*	*25.01*	*53.68*	*30.18 ± 0.25*
2	**1.13**	**1.06**		12.47 ± 0.35		41.76 ± 0.94				*72.29*	*25.01*	*53.68*	*30.18 ± 0.24*
3	**1.11**	**1.19**		12.47 ± 0.36		41.76 ± 0.94							*30.18 ± 0.24*
4	**1**	1.47	42.66 ± 0.80			41.62 ± 1.00				*72.05*	*24.93*	*53.52*	*30.10 ± 0.26*
5	1.27	**1.07**	40.47 ± 7.25	12.56 ± 0.37		41.80 ± 0.96				*72.35*	*25.03*	*53.72*	*30.20 ± 0.24*
6	**1.17**	**1.06**		12.47 ± 0.35		41.73 ± 0.96	*62.35 ± 1.47*			*72.23*	*24.99*	*53.64*	*30.16 ± 0.24*
7	**1.14**	**1**		12.47 ± 0.40		41.75 ± 1.04			*75.42 ± 0.71*	*71.96*	*24.9*	*53.46*	*30.07 ± 0.24*
8	2.88		small	11.4874				*23.2748*	*79.89 ± 3.91*	*75.11*	*25.95*	*55.56*	*31.12 ± 2.89*
9	1.54		43.42 ± 0.58	11.4874			*63.33 ± 3.45*	*23.2748*		*70.97*	*24.57*	*52.8*	*29.74 ± 0.50*
10	1.46		43.34 ± 0.65	11.4874	55.45 ± 1.58			*23.2748*					*small*
			42.82 ± 1.06	12.241		**41.75 ± 1.46**		*22.126*		*76.112*	*26.284*	*56.228*	*31.454*

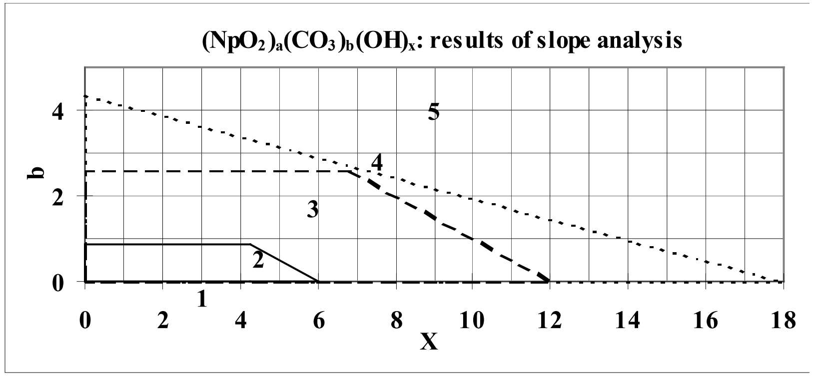


Figure [84MAY]-6 Possible first dissociated complex of Np(VI) during the titration of $NpO_2(CO_3)_3^{4-}$ with $HClO_4$. This is a schematic graphical representation of the slope analysis results (table [84MAY]-5). Following the same hypothesis as in the table [84MAY]-5, b and x can have integer values inside the geometrical domains for a = 1 (line), 2 (dashed line), 3(small dashed line). The size of the corresponding geometrical domain is due to uncertainty (on the graphical determination of the slopes). It is assumed that only one dissociated complex is formed, which is a rough approximation: it gives no information on the minor specie, it is a guide line to choose the species for curve fitting.

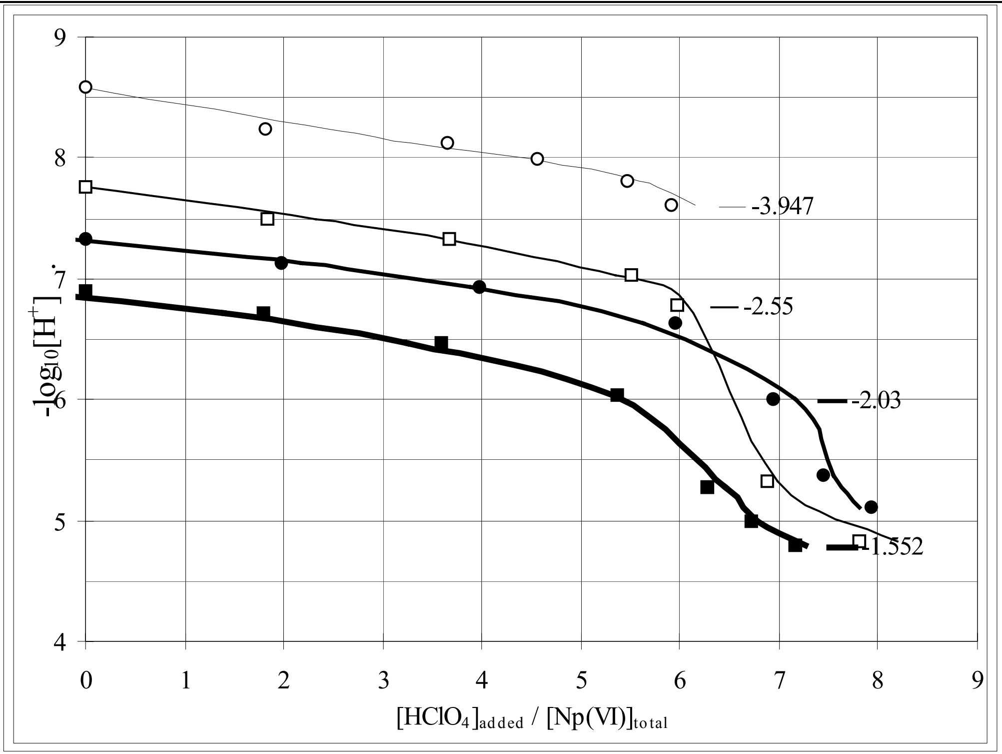
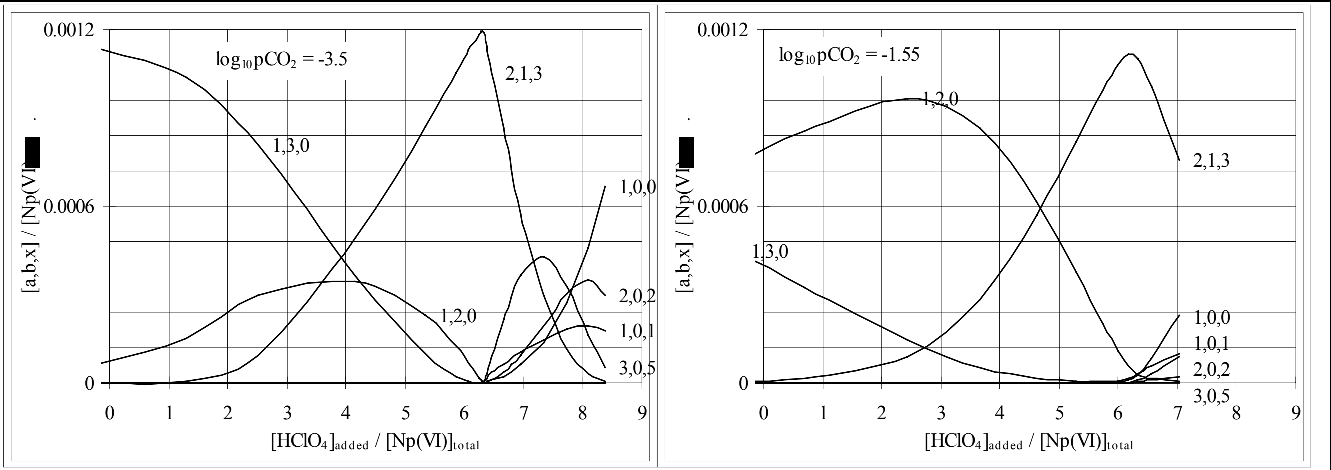


Figure [84MAY]-7 Potentiometric titration of $NpO_2(CO_3)_3^{-4}$ at different CO_2 partial pressures. The experimental points are those of the table [84MAY]-4. The numbers on the figure are $\log_{10}P_{CO_2}$ (atm). Theoretical curves correspond to the model proposed in the publication [84MAY]: it is the fit 2 of the table [84MAY]-5.



Figures [84MAY]-8 Speciation during titration of $NpO_2(CO_3)_3^{-4}$ ([84MAY]-7). These theoretical curves correspond to the [84MAY] model proposed by the author (and not accepted by this review): it is the fit 2 of the table [84MAY]-5.

Some of the chemical conditions of the above electrochemical measurements are similar to the chemical conditions of the potentiometric titration reported in this [84MAY] same publication; but in the later the results cannot be plotted on a single curve as a function of $[CO_3^{-2}]$. Since the total concentration of Np(VI) (about 1 mM) is also certainly higher, this is an evidence of formation of at least one polymeric Np(VI) complex containing some hydroxide anions. Speciation calculation or curve fitting, indicates that the known hydroxide Np(VI) complexes cannot be this (these) intermediary complex(es). This publication is then the first (and practically only) experimental evidence of the formation of (at least) one new polymeric Np(VI)-OH complex that also possibly contains some carbonate ligands. Further more, a straightforward graphical interpretation (table [84MAY]-5, figure [84MAY]-6) of the shift of the titration curve as a function of the carbonic gas partial pressure, indicates that the first dissociated complex could typically be one the following species $(NpO_2)_2CO_3(OH)_3^-$, $(NpO_2)_3(OH)_7^-$ or $(NpO_2)_3(OH)_8^{-2}$ (the corresponding Uranium ones are stable [92GRE/FUG] or have been recently proposed [95PAL/NGU]), or several other ones: the slope of the experimental titration curves at the half reaction point, as well as curve fitting results (table [84MAY]-5) agree with this conclusion. The graphical interpretation relies on the $-\log_{10}[H^+]$ value about the half point reaction:

$$-\log_{10}[H^+] = \log_{10}K + s_C \log_{10}P_{CO_2} + s_{Np} \log_{10}[Np]_t + \log_{10}f(eq)$$

where $s_C = \frac{b'}{-y'}$, $s_{Np} = \frac{a'-1}{-y'}$, a', b', x' and K are deduced from the notation of the author who uses $\beta_{a,b,x}$, the constant of the following equilibrium

$$a\ NpO_2^{+2} + b\ CO_{2(g)} + (b + x)\ H_2O \Leftrightarrow (a,b,x) + y\ H^+$$

where (a,b,x) is $(NpO_2)_a(CO_3)_b(OH)_x^{2a-2b-x}$, $y = 2b + x$

as indicated above, for chemical reasons this review preferred to refer to the starting complex, (1,3,0) rather than to the free cation, (1,0,0): $\beta'_{a,b,x} = \beta_{a,b,x} / (\beta_{a°,b°,x°})^{a'}$ was then used.

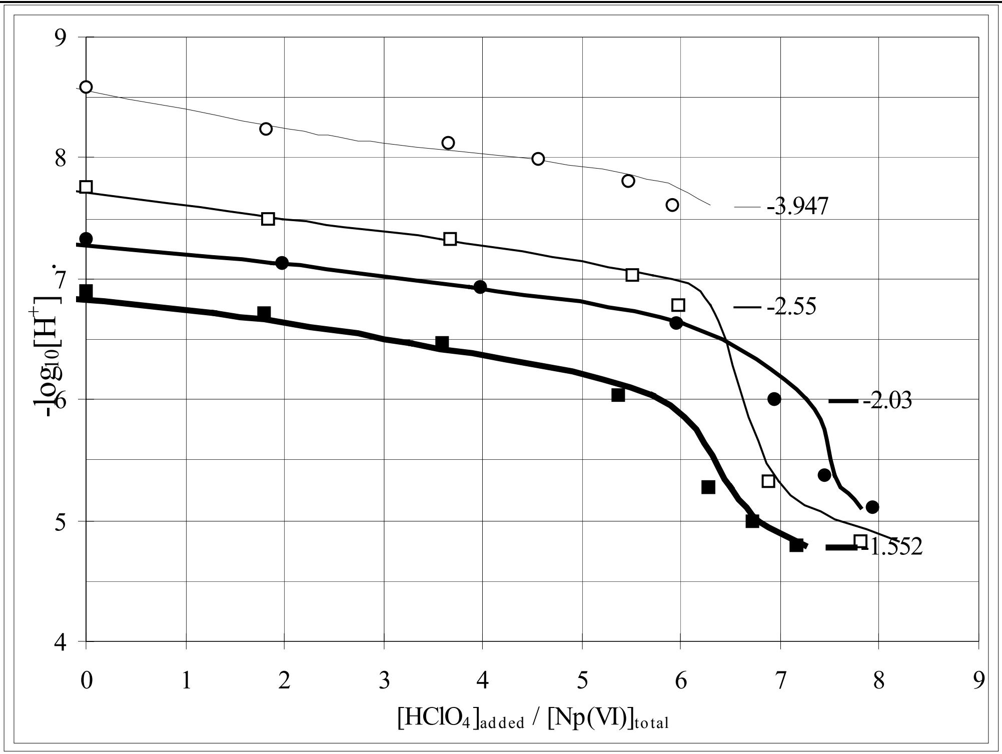
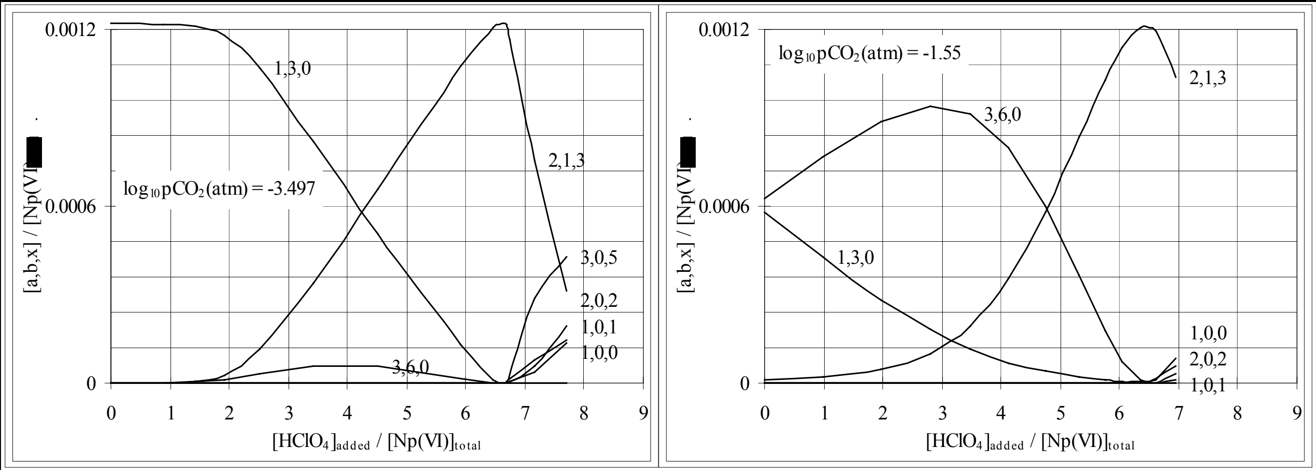
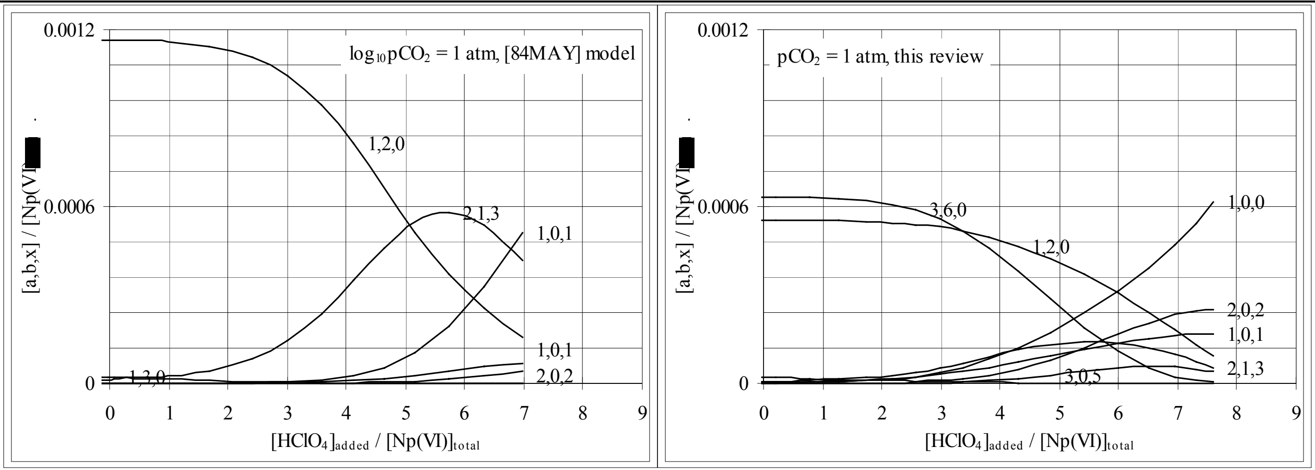


Figure [84MAY]-9 Potentiometric titration of $NpO_2(CO_3)_3^{-4}$ at different CO_2 partial pressures. The experimental points are those of the table [84MAY]-4. The numbers on the figure are $\log_{10}P_{CO_2}$ (atm). Theoretical curves correspond to the fit 5 of the table [84MAY]-5, performed by Maya; but that he finally excluded..



Figures [84MAY]-10 Speciation during titrations of $NpO_2(CO_3)_3^{-4}$ (figure [84MAY]-9) These theoretical curves correspond to the fit 5 (table [84MAY]-5) also performed by Maya; but that he finally excluded.



Figures [84MAY]-11: Speciation at P_{CO_2} = 1 atm, I = 1 M $NaClO_4$, during titration of $NpO_2(CO_3)_3^{-4}$, predicted with both models (figures [84MAY]-7 and 9). $NpO_2(CO_3)_2^{-2}$ stability proposed by the author ([84MAY] model) is in opposition with later direct (spectrophotometric) experimental qualitative observation at P_{CO_2} = 1 atm, I = 3 M [86GRE/RIG, 89RIG] (see text), as already stated in [86GRE/RIG].

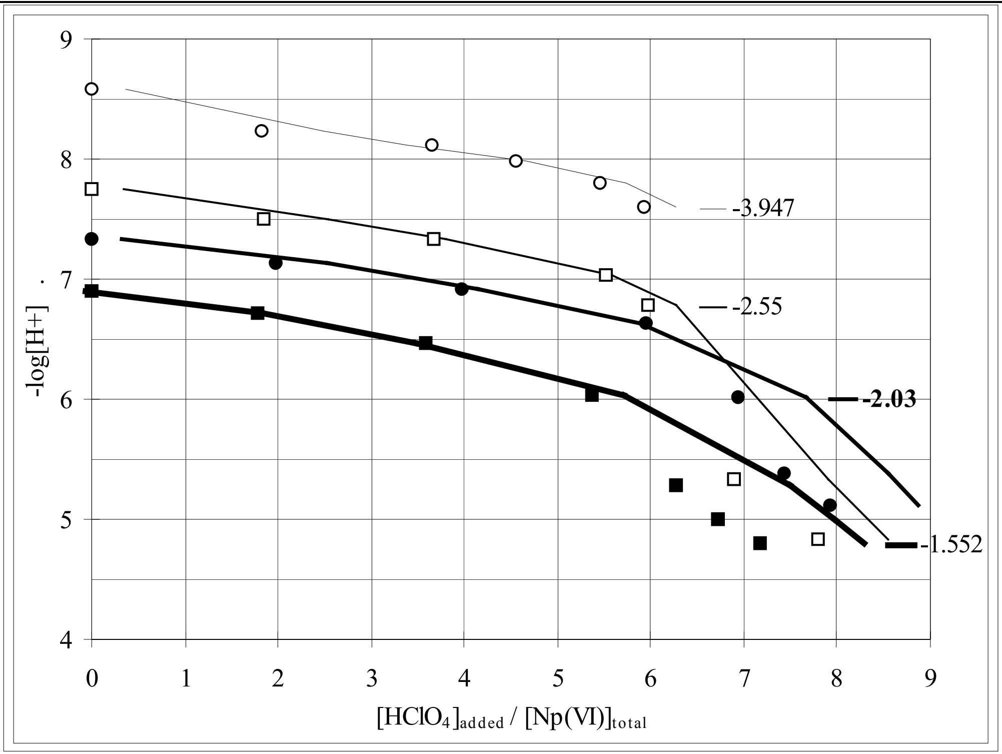


Figure [84MAY]-12 Potentiometric titration of $NpO_2(CO_3)_3^{-4}$ at different CO_2 partial pressures. The experimental points are those of the table [84MAY]-4. The numbers on the figure are $\log_{10}P_{CO_2}$ (atm). Theoretical curves correspond to the model proposed by this review, where (3,6,0) and (2,1,3) formation constants are fitted only on the 3 first experimental data at $\log_{10}P_{CO_2}$ = -1.552 and -3.5 respectively, since the other data were certainly in (very) oversaturated conditions.

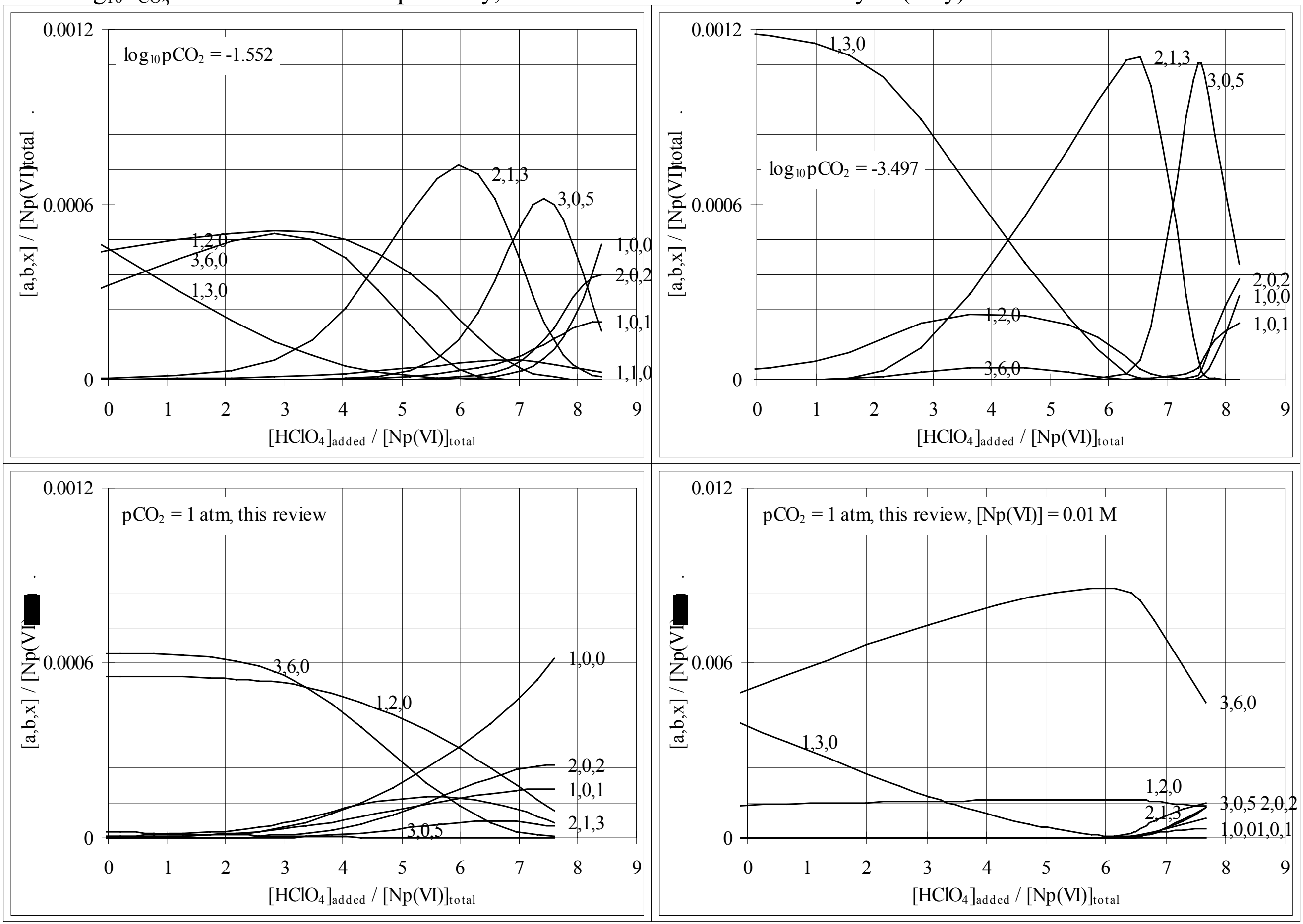


Figure [84MAY]-13 Speciation during titration of $NpO_2(CO_3)_3^{-4}$. These theoretical speciation curves correspond to the model of the above figure. Note the 3,6,0 (fitted) formation constant (i) strongly rely on the 1,2,0 and 1,3,0 formation constants values (that are taken from the data selected by this review as estimated from [77SIM, 89RIG, 95OFF/CAP and 97VIT/CAP] independent measurements, (ii) while it is virtually independent of the (2,1,3) fitted value. Higher P_{CO_2} (2 bottom figures) and total Np(VI) concentration (last figure) stabilise $(NpO_2)_3(CO_3)_6^{-6}$ species and would have then be better conditions to check its stoichiometry and formation constant; but these chemical conditions were not used by Maya.

where $(a°,b°,x°) = (1,3,0)$, $y° = 6$
then $a' = a / a° = a$, $b' = b - a'\ b° = b - 3$ and $y' = y - a'\ y° = y - 6$ $(y' < 0)$.
K is a constant: $-y' \log K = \lg \beta'_{a,b,x} + \log a' + (a' - 1) \log a° = \lg \beta'_{a,b,x} + \log a'$.
f(eq) is a function of the equivalent of acidity added, $eq = [HClO_4]_{added} / [Np]_t$.
$-y' \log f(eq) \approx - \log(a\ eq /(-y')) - (a'/ y') \log(1 + a\ eq / y')$ $(y' <0)$ it is an approximation since it is assumed that all the added acid is only used to dissociate the starting species, $(a°,b°,x°) = (1,3,0)$, into (a,b,x).

The $s_C \log_{10}P_{CO_2}$ term of the above formula is used for graphical interpretation (namely to estimate the ratio, b'/y', of CO_2 exchanged per H^+). The same type of qualitative information could certainly have been performed by using the s_{Np} $\log_{10}[Np]_t$ term (namely the degree of polynuclearity deduced from the ratio, (a'-1)/y', of polymerisation per H^+) if the author had varied $[Np]_t$. The slopes of the experimental curves were also used; their theoretical values are calculated with:

$$s_{pH} = \left(\frac{\partial\left(-\log_{10}\left[H^+\right]\right)}{\partial eq}\right)_{[M]_t, P_{CO_2}} = \frac{-a'n(n-1+a')}{(n-1)y'^2 \ln 10}$$

where $n = \frac{-y'}{a\,eq}$ has the same definition as in the table [84MAY]-5.

Graphical analysis (table [84MAY]-5 and figure [84MAY]-6) indicates that many possible complexes could be the first major dissociated one. Curve fitting results agree with this conclusion if we accept to consider not only the best fit; but also those, that are in a reasonable confidence interval (typically 1.96 Σ_{min} or even less). The fitting results proposed by Maya (fit 2 of the (table [84MAY]-5) is one among the many possible ones that give quite reasonable results. It is not the best fit according to his own criteria: (either Σ^2, the least square sum or $\Sigma / \sqrt{n-p}$, where n is the number of experimental measurements, and p the number of fitted parameters). This review accepts the numbers he proposed; but only as possible maximum values and (as already explained) for the equilibria corresponding to $\beta'_{a,b,x}$ and not $\beta_{a,b,x}$. The speciation (figure [84MAY]-8 and 10) calculated with this [84MAY] model (set of intermediary complexes) and with another one, agrees with the above a priori discussion (to limit the discussion, this review considered species proposed or suggested for Uranium by this series of review [92GRR/FUG] or recently [95PAL/NGU]):

- NpO_2^{+2} was always a minor species, one cannot then rely on the fitted value of its formation constant, $\beta_{1,0,0}$, and then on the formation constant of the limiting complex, $\beta_3 = 1 / \beta_{1,0,0}$ (i.e., since $NpO_2(CO_3)_3^{-4}$ is the starting species, $\beta_{1,0,0}$ is its overall dissociation constant). The uncertainty is then more important on $\beta_{a,b,x}$ than on $\beta'_{a,b,x}$.
- Any reasonable value for the formation constant of $NpO_2CO_{3(aq)}$ indicates that these species should certainly not be disregarded at the end of the titration using the highest CO_2 partial pressure (figures [84MAY]-10 and 11); unfortunately Maya did not report any fitting value for this species (he even neither fixed its formation constant). This is another reason to reject the fitted formation constants of all the species that are only formed at the end of the titration (figures [84MAY]-8 and 10).
- At least two intermediary complexes are needed to account for the experimental results. Maya [84MAY] have chosen $(NpO_2)_2CO_3(OH)_3^{-1}$ and $NpO_2(CO_3)_2^{-2}$. He excluded $(NpO_2)_3(CO_3)_6^{-6}$; but, despite what he said it is not clearly supported by his own curve fitting results (table [84MAY]-5, fit 5).
- Curve fitting results cannot exclude the formation of $(NpO_2)_3(OH)_7^-$ or $(NpO_2)_3(OH)_8^{-2}$ (table [84MAY]-5, fits 6, 9 and 10). It is not even clear whether $(NpO_2)_2CO_3(OH)_3^-$ has to be included in the model or not (table [84MAY]-5, fit 7).
- If the formation constants of $NpO_2(CO_3)_2^{-2}$ and $(NpO_2)_3(CO_3)_6^{-6}$ are fitted together, it appears that these two numbers are strongly correlated (as already mentioned, if $[Np]_t$ had been varied, this correlation should have vanished). This review then fixed one of them to the value estimated from the other part of this publication (electrochemistry). This gave a too poor fit. Adding $(NpO_2)_2CO_3(OH)_3^-$ to the model improved then the fit (table [84MAY]-5, fit 2 to7). As already said, adding $(NpO_2)_3(OH)_7^-$ or $(NpO_2)_3(OH)_8^-$ instead of $(NpO_2)_2CO_3(OH)_3^{-1}$ still gives reasonable fit. In fact the 3 species (or at least 2 of them) could exist; but there were not enough data in the correct chemical conditions to fit all their formation constants together (they are too much correlated to obtain meaningful results).
- The fitted value of the$(NpO_2)_3(CO_3)_6^{-6}$ formation constant, is also consistent with later work [86GRE/RIG, 89RIG] showing that $(NpO_2)_3(CO_3)_6^{-6}$ predominates at high CO_2 partial pressure (figures [84MAY]-11).
- This review also included as fixed parameters, the formation constants of the other species (NpO_2^{+2}, $NpO_2CO_{3(aq)}$ and $NpO_2(CO_3)_2^{-2}$) determined from the other part of this publication [84MAY]; but this always gave poor fitting results. $NpO_2CO_{3(aq)}$ is (as already said) an important species only at the end of the titration at the highest P_{CO_2}: the value attributed to its formation constant is then quite correlated to those of the minor species that are formed in these conditions, specially for NpO_2^{+2} and then β_3 (as explained above), and it does not change much the other fitting results. Experimental data at $P_{CO_2} = 1$ atm would have allow to determine the formation constant of $NpO_2(CO_3)_2^{-2}$.
- This review also tried to use as fixed value, β_3 (the formation constant of $NpO_2(CO_3)_3^{-4}$) determined from the [77SIM] and [95OFF/CAP] works (selected by this review) and then to fit $\beta_{3,6,0}$ and β_1 (the formation constants of $(NpO_2)_3(CO_3)_6^{-6}$ and $NpO_2CO_{3(aq)}$ respectively) from only the data where these species predominate (i.e. at the highest P_{CO_2} at the end and the beginning of the titration respectively) and finally to fit iteratively $\beta_{2,1,3}$ (the formation constant of $(NpO_2)_2CO_3(OH)_3^{-1}$) in the same way (i.e. at the lowest P_{CO_2}). This is equivalent to give higher weighting factors to the corresponding data and this gave reasonable values; but the fit is still quite poor. Finally this last data treatment was modified (see below) to propose data.

Following the [84MAY] author, several interpretations (several sets of $(NpO_2)_a(CO_3)_b(OH)_x^{2a-2b-x}$ species) can account for the [84MAY] potentiometric data in 1 M $NaClO_4$ aqueous solution: quantitative interpretation showed evidence of at least one new polymeric hydroxide complex of Np(VI) (as mentioned above); but not a unique stoichiometry could be proposed from only these [84MAY] experimental data when only using statistical approach to compare possible models.

There is evidence of $(NpO_2)_3(CO_3)_3^{-6}$ in similar chemical conditions from later published works [86GRE/RIG, 89RIG], and this species could certainly not be disregarded in the buffering region of the [84MAY] titration at the highest carbonic gas partial pressure. To be consistent with published data this review used fixed β_i values ($NpO_2(CO_3)_i^{2-2i}$ formation constants) as selected by this review to calculate $(NpO_2)_3(CO_3)_3^{-6}$ formation constant $\beta_{3,6}$, from the first three data at highest P_{CO_2} from this work [84MAY], because high P_{CO_2} stabilises $(NpO_2)_3(CO_3)_3^{-6}$ and the end of the titration was certainly performed in oversaturated conditions. For similar reasons $(NpO_2)_2CO_3(OH)_3^-$ formation constant was calculated from the first three data at lowest P_{CO_2} still using the same β_i fixed values, and now also fixing the $\beta_{3,6}$ value previously estimated. This data treatment was repeated iteratively. Uncertainty was estimated as $\log_{10}\beta'_{3,6,0,}$ or $\log_{10}\beta'_{2,1,3}$ values that multiply the square root of the least square sum, by 2.96. This gave numerical results (see below) consistent with previous statistical data treatment, the other potentiometric data (those not used to estimate $\beta'_{3,6,0,}$ nor $\beta'_{2,1,3}$ values) were consistent with this model in the buffering region, while about the equivalent point discrepancy can be attributed to slow precipitation (figure [84MAY]-12). According to this model, at $\log_{10}P_{CO_2} = -1.55$ (figure [84MAY]-13) the limiting complex ($NpO_2(CO_3)_3^{-4}$) is partially dissociated into $(NpO_2)_3(CO_3)_3^{-6}$ and $NpO_2(CO_3)_2^{-2}$ even in the initial aqueous solution, further dissociation lead to $(NpO_2)_2CO_3(OH)_3^-$ and then to many other species in oversaturated conditions. It is clear (see the same set of figures) that higher P_{CO_2} would have give simpler speciation (and then data treatment) eliminating the mixte polynuclear species. Varying Np(VI) total concentration (see the set same of figure) would have been the only way to allow to vary the $[(NpO_2)_3(CO_3)_3^{-6}]$ / $[NpO_2(CO_3)_2^{-2}]$ ratio because in this two species the Np(VI)/CO_3 stoichiometric ratio is 2. It would have then been the only way to allow estimation of both formation constants for these two species. Unfortunately Maya did not vary $[Np(VI)]_{total}$, possibly because he did not clearly understand qualitative interpretation of mass action law for polynuclear species. At $\log_{10}P_{CO_2} = -3.50$ (figure [84MAY]-13) the limiting complex was not or only partially dissociated in the chemical conditions used to estimate $\beta'_{2,1,3}$ value (beginning of the titration), and this explains it was more difficult to obtain this value than the $\beta'_{3,6,0,}$ one. Now coming back to our and Maya's previous curve fitting results (figure [84MAY]-7 to 11), speciation also explains why it was not possible to extract clear conclusion from only statistical analysis.

First as already mentioned in several ways there is mathematically no way to fit together $(NpO_2)_3(CO_3)_3^{-6}$ and $NpO_2(CO_3)_2^{-2}$ formation constants because their concentration ratio was not allowed to vary in the experimental conditions used by Maya.

Second the species that predominates the most (i.e. in most chemical conditions) for any (reasonable) model is $(NpO_2)_2CO_3(OH)_3^-$, it will then have the major influence on the statistical fitting criterion, unfortunately the majority of the corresponding conditions are certainly oversaturated and low weight should have been given to these data. As a consequence curve fitting usually overestimates $(NpO_2)_2CO_3(OH)_3^-$ stability, and this makes this species being the major dissociated specie even at the beginning of the titration where in turn $(NpO_2)_3(CO_3)_3^{-6}$ and $NpO_2(CO_3)_2^{-2}$ contributions are not enough for the statistical criterion used.

Finally this review proposes the following bolded data (the other ones are shown only for comparison, uncertainty was estimated by this review):

$\log_{10}\beta'_{3,6,0,}$		=	**42.82**	±	**1.06**	**for $3\ NpO_2(CO_3)_3^{-4} + 6\ H^+ \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6} + 3\ CO_{2(g)} + 3\ H_2O$**
			40.47	±	7.25	could be estimated from statistical analysis
			42.66	±	0.80	calculated and excluded by the author [84MAY]
then	$\log_{10}(\beta_{3,6}/\beta_3^3)$	=	**-8.81**	±	1.07	for $3\ NpO_2(CO_3)_3^{-4} \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6} + 3\ CO_3^{-2}$
		or	-11.15 ± 7.25 and -8.96 ± 0.82 respectively.			
	$\log_{10}\beta_{3,6,0,}$	=	**-51.54**	±	1.62	for $3\ NpO_2^{+2} + 6\ CO_{2(g)} + 6\ H_2O \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6} + 12\ H^+$
		or	-53.89	±	7.35 and -51.70 ± 1.46 respectively.	
	$\log_{10}\beta_{3,6,}$	=	**51.70**	±	1.66	for $3\ NpO_2^{+2} + 6\ CO_3^{-2} \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6}$
		or	49.35	±	7.36 and 51.45 ± 1.51 respectively.	
$\log_{10}\beta'_{2,1,3}$		=	**41.75**	±	**1.46**	**for $2\ NpO_2(CO_3)_3^{-4} + 7\ H^+ \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 5\ CO_{2(g)} + 2\ H_2O$**
			41.62	±	1.00	could be estimated from statistical analysis
			41.76	±	0.94	proposed by the author [84MAY]
then	$\log_{10}K/\beta_3^2$	=	**-44.29**	±	**0.48**	for $2\ NpO_2(CO_3)_3^{-4} + 3\ H_2O \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 5\ CO_3^{-2} + 3\ H^+$
		or	-44.28	±	0.99 and -44.42 ± 1.04 respectively.	
	$\log_{10}\beta_{2,1,3}$	=	**-21.16**	±	**1.67**	for $2\ NpO_2^{+2} + CO_{2(g)} + 4\ H_2O \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 5\ H^+$
		or	-21.15	±	1.24 and -21.29 ± 1.29 respectively.	
	$\log_{10}K$	=	**-3.95**	±	**1.67**	for $2\ NpO_2^{+2} + CO_3^{-2} + 3\ H_2O \Leftrightarrow (NpO_2)_2CO_3(OH)_3^- + 3\ H^+$
		or	-3.94	±	1.25 and -4.08 ± 1.29 respectively.	
$\log_{10}\beta'_{1,2,0}$		<	12.47			**for $NpO_2(CO_3)_3^{-4} + 2\ H^+ \Leftrightarrow NpO_2(CO_3)_2^{-2} + CO_{2(g)} + H_2O$**
			12.47	±	0.47	proposed by the author [84MAY]
			12.24			selected by this review from independent data [97VIT/CAP]
			11.49			calculated by this review from the [84MAY] redox measurements
			12.70			proposed by the author [84MAY] from his redox measurements
then	$\log_{10}(\beta_2/\beta_3)$	<	-4.74			for $NpO_2(CO_3)_3^{-4} \Leftrightarrow NpO_2(CO_3)_2^{-2} + CO_3^{-2}$
		or	-4.74	±	0.36, **-4.97**, -5.72 and -4.51 respectively.	
	$\log_{10}\beta_{1,2,0}$	<	-18.98			for $NpO_2^{+2} + 2\ CO_{2(g)} + 2\ H_2O \Leftrightarrow NpO_2(CO_3)_2^{-2} + 4\ H^+$
		or	-18.98	±	0.54, **-19.21**, -19.97 and -18.85 respectively.	
	$\log_{10}\beta_2$	<	15.43			for $NpO_2^{+2} + 2\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_2^{-2}$
		or	15.43	±	0.55, **15.20 ± 0.54**, 14.45 and 15.6 respectively.	

This review also proposes maximum possible values for the formation constants of the following species, this does not mean that they really exist; but since these calculated values are similar to those selected for Uranium [92GRE/FUG], they could as well exist as minor species during the [84MAY] titration

$\log_{10}\beta'_{3,0,7}$ $<$ 63.33 for $3\ NpO_2(CO_3)_3^{-4} + 11\ H^+ \Leftrightarrow (NpO_2)_3(OH)_7^- + 9\ CO_{2(g)} + 2\ H_2O$

62.35 ± 1.47 calculated and excluded by the author [84MAY]

then $\log_{10}\beta_{3,0,7}/\beta_3^3$ $<$ -91.53 or =-92.51±1.57 for $3\ NpO_2(CO_3)_3^{-4} + 7\ H_2O \Leftrightarrow (NpO_2)_3(OH)_7^- + 3\ CO_3^{-2} + 7\ H^+$

then $\log_{10}\beta_{3,0,7}$ $<$ -31.03 or =-32.01±1.91 for $3\ NpO_2^{+2} + 7\ H_2O \Leftrightarrow (NpO_2)_3(OH)_7^- + 7\ H^+$

$\log_{10}\beta'_{3,1,3}$ $<$ 75.42 for $3\ NpO_2(CO_3)_3^{-4} + 13\ H^{+-} \Leftrightarrow (NpO_2)_3CO_3(OH)_3^+ + 8\ CO_{2(g)} + 5\ H_2O$

75.42 ± 0.71 proposed by the author [84MAY]

then $\log_{10}K/\beta_3^3$ $<$ -62.24 or =-62.84±0.86 for $3\ NpO_2(CO_3)_3^{-4}+3\ H_2O \Leftrightarrow (NpO_2)_3CO_3(OH)_3^+ + 8\ CO_3^{-2} + 3\ H^+$

$\log_{10}\beta_{3,1,3}$ $<$ -18.94 or =-18.94±1.41 for $3\ NpO_2^{+2} + CO_{2(g)} + 4\ H_2O \Leftrightarrow (NpO_2)_3CO_3(OH)_3^+ + 5\ H^+$

$\log_{10}K$ $<$ -1.73 or =-1.73±1.42 for $3\ NpO_2^{+2} + CO_3^{-2} + 3\ H_2O \Leftrightarrow (NpO_2)_3CO_3(OH)_3^+ + 3\ H^+$

The $(NpO_2)_3CO_3(OH)_3^+$ species should rather be written $(NpO_2)_3O(OH)_2HCO_3^+$ as for Uranium [92GRE/FUG].

The $(UO_2)_3(OH)_8^{-2}$ species was not selected for [92GRE/FUG]; but it was recently proposed again [95PAL/NGU] and the corresponding $(NpO_2)_3(OH)_8^{-2}$ formation constant possible maximum value calculated by this review indicates that this species could also have been a minor species during the [84MAY] titration

$\log_{10}\beta'_{3,0,8}$ $<$ 55.45 for $3\ NpO_2(CO_3)_3^{-4} + 10\ H^+ \Leftrightarrow (NpO_2)_3(OH)_8^{-2} + 9\ CO_{2(g)} + H_2O$

The $(UO_2)_3(OH)_{10}^{-4}$ species was not selected [92GRE/FUG]; but it was recently proposed again [95PAL/NGU] and the corresponding $(NpO_2)_3(OH)_{10}^{-4}$ formation constant possible maximum value calculated by this review indicates that this species could certainly not be detected during the [84MAY] titration

[84THO/NAS]

Thompson M.E., Nash K.L., Sullivan J.C. Complex of Hydrogen Peroxide with Dioxoactinide(VI) Species in Aqueous Carbonate and Bicarbonate Media. Formation of An(VI)-H_2O_2 Complexes. Israel J. Chem., 25 (1985) 155-158.

This work reports kinetic data, mostly on Uranium (it was not used in the Uranium [92GRE/FUG] volume of this series), and suggests analogue transient species of Np(VI). It was not used in this review.

[84VAR/BEG]

Varlashkin P.G., Begun G.M., Hobart D.E. Spectroscopic and electrochemical investigations of neptunium and plutonium in concentrated aqueous carbonate and carbonate-hydroxide solutions. DOE/ER/04447-168 (Dec. 1984) 5-13.

This report is a prepublication of [84VAR/HOB]

[84VAR/HOB]

Varlashkin P.G., Hobart D.E., Begun G.M., Peterson J.R. *Electrochemical and spectroscopic studies of neptunium in concentrated aqueous carbonate and carbonate-hydroxide solutions*. Radiochim. Acta, 35 (1984) 91-96.

This publication reports a value of the Np(VI)/Np(V) redox potential in 2M $NaCO_2$ aqueous solution. No indication is given about the calibration of the reference (saturated calomel) electrode neither the junction potential. This could explain the observed deviation from the careful previous work of [77SIM]. It seems that NaOH addition to a solution of the Np(VI) carbonate limiting complex, $NpO_2(CO_3)_3^{-4}$, could induce the reduction of Np(VI) to Np(V) possibly by water.

[84VOL/KAP]

Volkov Yu.V., Kapshikov I.I. *Some aspects of the crystal chemistry of complex compounds of actinides in higher oxidation states*. Radiokhim., 26, 3 (1984) 361-370. English translation Sov. Radiochem. 26, 3 (1984) 341-349.

This publication is an interesting review paper on the stability of some carbonate and other actinide solid compounds. It does not contain any thermodynamic data.

[85SCH/FRI]

Schreiner, F., Friedman, A.M., Richards, R.R., Sullivan, J.C *Microcalorimetric measurement or reaction enthalpies in solutions of uranium and neptunium compounds*, J. Nucl. Mater., 130 (1985) 227-233.

This work reports Uranium and Neptunium calorimetric titration from Na_2SO_4 to Na_2CO_3 or $NaHCO_3$ aqueous solutions at 25°C, I = 1.6 M for $[U(VI)]_t$ typically 50 µM (before dilution du to the titration). It was certainly similar conditions for Neptunium. The Uranium part of this work has already been examined in this series of reviews [92GRE/FUG]. The same reinterpretation (as in [92GRE/FUG]) was used by the present review. The authors [85SCH/FRI] reported enthalpy changes for

$$UO_2^{+2} + 2\ CO_3^{-2} \Leftrightarrow UO_2(CO_3)_2^{-2}$$

and for M = U and Np $$MO_2^{+2} + 3\ CO_3^{-2} \Leftrightarrow MO_2(CO_3)_3^{-4}$$

"The technical quality of the enthalpy data seem[ed] to be satisfactory" to Grenthe et al. [92GRE/FUG]; but they found that "the two main reactions taking place under the conditions of [this [85SCH/FRI] publication] are", for uranium.

$$UO_2SO_{4(aq)} + 2\ CO_3^{-2} \Leftrightarrow \frac{1}{3}(UO_2)_3(CO_3)_6^{-6} + SO_4^{-2}$$

$$UO_2SO_{4(aq)} + 3\ CO_3^{-2} \Leftrightarrow UO_2(CO_3)_3^{-4} + SO_4^{-2}$$

and they used the data of this [85SCH/FRI] publication, without any ionic strength correction [85SCH/FRI]. So this review accept the value

$$\Delta_r H_m(I = 1.6\ M\ Na_2SO_4 + Na_2CO_3) = -50 \pm 2\ kJ.mol^{-1}$$

for the reaction $$NpO_2SO_{4(aq)} + 3\ CO_3^{-2} \Rightarrow NpO_2(CO_3)_3^{-4} + SO_4^{-2}$$

[86GRE/RIG]

Grenthe, I., Riglet, C., Vitorge, P. *Studies of metal-carbonate complexes: 14. Composition and equilibria of trinuclear neptunium(VI)- and plutonium(VI)-carbonates complexes*, Inorg. Chem., 25 (1986) 1679-1684.

Dissociation of the carbonate limiting complexes of Np(VI) and Pu(VI), $MO_2(CO_3)_3^{-4}$, in 3 M $NaClO_4$ was studied in aqueous solution at T = 22 ± 1 °C, by using a spectrophotometric technique. Glass electrode with zero junction potential was correctly calibrated in concentration units ($-\log_{10}[H^+]$). The aim of this work was mainly to show that as U(VI), Np(VI) and Pu(VI) form a trinuclear complex in concentrated bicarbonate media: this was effectively demonstrated. This review then agrees with the conclusion of this [86GRE/RIG] work and used the equilibrium constants measured by the authors. The original experimental data were published as supplementary materials. The Np(VI) ones are also in Riglet's thesis [89RIG]. From isobestic points and quantitative graphical interpretation the authors concluded that two species are enough to interpret the data. For constant total metal concentration, the measured molar absorbance was plotted on a single curve as a function of $[CO_3^{-2}]$ whatever the carbonic gas partial pressure used ($0.1 < P_{CO_2} < 1$atm). The authors [86GRE/RIG] then concluded that the major dissociated complex contains only CO_3^{-2} ligand: this is correct and matches the qualitative prediction made using [84MAY] Np(VI) potentiometric data as reinterpreted by this review (figure [84MAY]-11, in this Appendix). The stability of the dissociated complex increased with the total metal concentration: this is a direct experimental evidence that a polynuclear complex was formed (and then that the interpretation proposed earlier by Maya [84MAY] is incorrect). It was confirmed by the sensitivity analysis performed by the [86GRE/RIG] authors. The stoichiometry of the dissociated complex can readily be determined by using straightforward slope analysis. This graphical interpretation was used for Neptunium in [89RIG] (see the discussion on [89RIG] in this appendix). Sensitivity analysis performed in this [86GRE/RIG] publication showed, that the dissociation equilibrium is

$$3\ NpO_2(CO_3)_3^{-4} \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6} + 3\ CO_3^{-2}$$

The experimental data ($\log_{10}[CO_3^{-2}]$, $\log_{10}$(molar absorbance)) were graphically compared with theoretical curves calculated for constant total metal concentration, assuming that there was only one major soluble dissociated complex with different possible stoichiometry. This method allowed the determination of the constant of the above equilibrium. In the same way

for M = Np or Pu $\quad 2\ UO_2(CO_3)_3^{-4} + MO_2(CO_3)_3^{-4} + \Leftrightarrow (UO_2)_2MO_2(CO_3)_6^{-6} + 3\ CO_3^{-2}$

mixed equilibria were studied in the same conditions by using the same experimental procedure. The corresponding equilibrium constants were determined by using the same graphical method. They were already accepted in the Uranium volume of this series of review [92GRE/FUG]. This review then accepts the same values for the mixed complexes (THIS HAS TO BE CHECKED WITH BILL for Pu). For the mixed complexes, the carbonic acid constants were first changed in [92GRE/FUG] because the ones used in the [86GRE/RIG] original publication did not agree with their values recalculated by using the SIT formula. It was finally recognised (and corrected in [95SIL/BID]) that this (rather small) discrepancy between the carbonic acid equilibrium constants (table[84MAY]-3 in this appendix) was mainly due to poor accuracy of the $\varepsilon(CO_3^{-2},Na^+)$ and $\varepsilon(HCO_3^-,Na^+)$ values and numerical artefacts (not enough digit in these ε values).

The $(UO_2)_3(CO_3)_6^{-6}$ formation constant was calculated in the [92GRE/FUG] Uranium review from the data of the same authors published elsewhere and from the other publications where the trinuclear species was a major species; but that they reinterpreted [92GRE/FUG] since the authors did not take it into account. Similarly, this review accepts the value of the equilibrium constants determined in this [86GRE/RIG] publication (THIS HAS TO BE CHECKED WITH BILL for Pu) and for Neptunium this review also used the $(NpO_2)_3(CO_3)_6^{-6}$ formation constant estimated from the [84MAY] publication as reinterpreted by this review in this appendix, since it was the major species during one of the titration (figure [84MAY]-10 in this appendix). See also the discussion on [89RIG] in this appendix for the Np(VI) data.

[86GRE/ROB]

Grenthe I., Robouch P., Vitorge P. *Chemical Equilibria in Actinide Carbonate Systems*. Actinide 85. Aix-en-Provence. J. Less. Common Metals, 122, 255-31 (1986)

For Np(VI), this publication reports some of the data published with more experimental details in [86GRE/RIG]. In addition the X-ray diffraction patterns of the $PuO_2CO_{3(cr)}$ and $NpO_2CO_{3(cr)}$ compounds are reported. They have the same structure as Rutherfordine, $UO_2CO_{3(cr)}$.

[86THE/JOV]

Thevenin T., Jove J., Madic C. *Crystal chemistry and ^{237}Np Mössbauer investigations of neptunyl(VI) carbonate NpO_2CO_3*. Actinide 85. Aix-en-Provence. J. Less. Common Metals, 121, 477-481 (1986)

This publication reports the X-ray diffraction patterns of the $NpO_2CO_{3(cr)}$ solid. It is consistent with the one simultaneously published in [86GRE/ROB]: both X-ray diffraction patterns were possibly registered on the same apparatus in the same laboratory; but the two samples were prepared independently. No thermodynamic data are published in this [86THE/JOV] work.

[88ULL/SCH]

Ullman, W.J., Schreiner, F. Calorimetric determination of the enthalpies of the carbonate complexes of U(VI), Np(VI), and Pu(VI) in aqueous solution at 25° C, Radiochim. Acta, 43 (1988) 37-44.

The Uranium part of this publication had already been examined [92GRE/FUG] in this series of reviews. It was noticed that it is essentially the same type of experimental study as the one described by Schreiner et al. in [85SCH/FRI]. To typically 1.5 ml Na_2SO_4 solution (ionic strength was initially 0.45 or 0.46 M) containing 0.0289 to 0.0447 M Np(VI), 0.1 to 1 M Na_2CO_3 aqueous solutions were added to obtain an excess of carbonate ion: 0.58 to 19.7 times the Np(VI) concentration. The Na_2CO_3 concentration was then 0.053 to 0.363 M. The value $\Delta_rH_m = -41.9 \pm 1.3$ kJ.mol^{-1} reported for the reaction

$$NpO_2^{+2} + 3\ CO_3^{-2} \Leftrightarrow NpO_2(CO_3)_3^{-4}$$

is different from the one proposed in [85SCH/FRI] apparently because it does not include here [88ULL/SCH] sulphate complexation: the authors subtracted the contribution of sulphate by measuring sulphate blank. This is then consistent with the interpretation of [85SCH/FRI] in this appendix, similarly to the Uranium data [92GRE/FUG]. As soon as the stoichiometric amount of carbonate was added, calorimetric measurements gave constant results. The authors [88ULL/SCH] concluded that the limiting carbonate complex, $NpO_2(CO_3)_3^{-4}$, was then formed: this is correct and this review then calculated by using the same data (those corresponding to an excess of carbonate)

$$\Delta_rH_m(I \approx 0.098 \text{ to } 0.135 \text{ M } Na_2SO_4 + 0.123 \text{ to } 0.363 \text{ M } Na_2CO_3) = -42.0 \pm 3.2 \text{ kJ.mol}^{-1}$$

where (following the [88ULL/SCH] authors) $\Delta H_{sulphate} = 22.5$ kJ.mol^{-1} for the dissociation of sulphate complexes, has been subtracted from the mean of the heat experimental data $\Delta H_3 = -64.48 \pm 2.29.$ kJ.mol^{-1}. This last value is not the same as in [85SCH/FRI] possibly because the starting sulphate solutions were not the same. The uncertainty on ΔH_3 is 1.96 standard deviation, and this review assumed that it was the same on $\Delta H_{sulfate}$. This is consistent with the value calculated by the author, so this review finally proposes the value of the author with their estimation of the uncertainty:

$$\Delta_rH_m(I \approx 0.098 \text{ to } 0.135 \text{ M } Na_2SO_4 + 0.123 \text{ to } 0.363 \text{ M } Na_2CO_3) = -41.9 \pm 3.2 \text{ kJ.mol}^{-1}$$

ΔH_3 measurements remain (within ± 2.3 kJ.mol^{-1}) constant, after the formation of the limiting complex. Since the contributions of Na_2SO_4 dilution and of Na_2CO_3 addition to the measured heat were subtracted with the blank, and since the number of mole of Np(VI) is constant in each series of titration, in each series of titration when an excess of Na_2CO_3 is used the only contributions to this (undetected) Δ_rH_m variation is [93GIF/VIT, 94GIF/VIT] the variation of

$$H^{exc}_{NpO_2(CO_3)_3^{-4}} = -R\ T^2 \left(\frac{\partial \ln \gamma_{NpO_2(CO_3)_3^{-4}}}{\partial T}\right)_P$$

$$= -R\ T^2 \ln 10 \left(-16\left(\frac{\partial D}{\partial T}\right)_P + \left(\frac{\partial \varepsilon_{NpO_2(CO_3)_3^{-4}}}{\partial T}\right)_P m_{NpO_2(CO_3)_3^{-4}}\right)_P$$

The variation of the Debye-Hückel term, D, contribution (used in this review: SIT) is 0.8 kJ.mol^{-1}, the contribution of the second virial term is then less than (2.3 + 0.8) = 3.1 kJ.mol^{-1} which corresponds to

$$|\varepsilon'_{VI}| = \left|\left(\frac{\partial \varepsilon_{NpO_2(CO_3)_3^{-4}}}{\partial T}\right)_P\right| < 0.018 \text{ kg mol}^{-1}\text{ K}^{-1}$$

For comparison: $\Delta\varepsilon'$ (= $\varepsilon'_{VI} - \varepsilon'_V$) = -0.0053 kg mol^{-1} K^{-1} was estimated from [95OFF/CAP] redox measurements. As already pointed out by the [88ULL/SCH] authors and for Uranium in [92GGRE/FUG], Δ_rH_m calculation from the experimental data does not depend on the equilibrium constants, since it relies on an overall titration and not on speciation variation in the course of the titration. For this reason, the measured heat value is directly an enthalpy of reaction. When plotting the heat measured before the end of titration (before the formation of the limiting complex), one does not find a linear variation with the amount of carbonate added: this is an evidence of formation of intermediary species. In these conditions one expects contribution of the trinuclear carbonate complex; but the [88ULL/SCH] authors did not use this interpretation; and it is not possible to choose between different models. Following [92GRE/FUG] reinterpretation for Uranium, the ΔH_2 value determined by the author, the

$$NpO_2^{+2} + 2\ CO_3^{-2} \Leftrightarrow \frac{1}{3}(NpO_2)_3(CO_3)_6^{-6}$$

equilibrium should also contribute to ΔH_2; but the ΔH_2 value measured for Neptunium is quite different from the corresponding Uranium or Plutonium values measured in the same [88ULL/SCH] work. This could be due to some experimental kinetic problems as noticed in [89RIG] in similar conditions, where Np(VI) kinetic behaviour was found to be different from the U(VI) or Pu(VI) one. This review then did not use the ΔH_2 value measured for Np(VI).

[89MOR/PRA1]

Moriyama H., Pratopo M. I., Higashi K. *The solubility and colloidal behaviour of neptunium(IV).* Sci. total environment. 83 (1989) 227-237

[89MOR/PRA2]

Moriyama H., Pratopo M. I., Higashi K. *The behaviour of neptunium under reducing conditions.* in High Level Radioactive Waste and Spent Fuel Management, (Slate, Kohout and Suzuki eds.) 2 p310 (1989).

[89RIG]

Riglet, C. *Chimie du neptunium et autres actinides en milieu carbonate*, Thesis, Université Paris 6, 17 march 1989, in French, also Report CEA-R-5535, Commissariat a l'Energie Atomique, Gif-sur-Yvette, France, 1990, 267p. for this reason sometimes refereed as [90RIG].

This thesis includes a spectrophotometric study of the dissociation of the Np(VI) carbonate limiting complex, that was published in [86GRE/RIG]. Dissociation of the Np(VI), carbonate limiting complex in 3 M $NaClO_4$ was studied in aqueous solution at T = 22 ± 1 °C. Glass electrode with zero junction potential was correctly calibrated in concentration units ($-\log_{10}[H^+]$). From isobestic points and quantitative graphical interpretation the author concluded that two species

Table [89RIG]-1 Graphical determination of the stoichiometry of the soluble complex in equilibrium with the Np(VI) limiting complex in 1 mM Np(VI) aqueous bicarbonate solutions: the limiting complex is $NpO_2(CO_3)^{-4}$. The unknown dissociated complex is $(NpO_2)_i(CO_3)_j^{2(i-j)}$. Absorbance measurements, A, at 670 and 700 nm were plotted versus $\log_{10}[CO_3)^{-2}]$ for each $[Np(VI)]_{total}$. The slope, P, of these type of curves at the half reaction point and their shift, p, versus $\log_{10}[Np(VI)]_{total}$, were used to calculate two theoretical (linear) relationships [89RIG] involving the stoichiometric coefficients, i and j: $j = a_n\, i + b_n$ (n = 1 and 2), where $a_1 = 3 - p$, $b_1 = p$, $a_2 = 3 + 0.5\, r\, P$, $b_2 = r\, p$

$$P = \left(\frac{\partial \log_{10}\left(A / [Np(VI)]_{total} \right)}{\partial \log_{10}\left[CO_3^{-2}\right]} \right)_{[Np(VI)]_{total}} , \quad p = \left(\frac{\partial \log_{10}\left[CO_3^{-2}\right]}{\partial \log_{10}[Np(VI)]_{total}} \right)_{A / [Np(VI)]_{total}} , \quad r = \frac{0.5 i\, \varepsilon_D + \varepsilon_L}{0.5 i\, \varepsilon_D - \varepsilon_L},$$

ε_D and ε_L are the molar absorbances of the dissociated and of the limiting complex. The [89RIG] original determination estimated graphically the slopes and the corresponding uncertainty. This review used linear regressions and the corresponding 1.96 σ. The result of both determinations is the same: i=3, j=6, the dissociated complex is then $(NpO_2)_3(CO_3)_6^{-6}$. The actual uncertainties on i and j are plotted on the figure [89RIG]-1. The theoretical values are here tabulated without uncertainty.

	r	P	b_2	a_2	b_1	a_1	i	j
670nm		0.405	-1.2	2.4	1.5	1.5	3	6
[89RIG]		0.33±0.05	-0.68±0.1	2.32±0.1	1.5±0.1	1.5±0.1	2.66±0.69	5.49±1.22
this review	-2.96	0.40±0.02	-1.18±0.06	2.41±0.03	1.51±0.11	1.49±0.11	2.92±0.40	5.86±0.81
700nm		0.346	-1.2	2.4	1.5	1.5	3	6
this review	-3.47	0.32±0.04	-0.95±0.04	2.53±0.02	1.51±0.11	1.49±0.11	2.37±0.27	5.04±0.56

were enough to interpret the data. For constant total metal concentration, the measured molar absorbance was plotted on a single curve as a function of $[CO_3^{-2}]$, whatever the carbonic gas partial pressure used ($0.1 < P_{CO_2} < 1$atm). This qualitative conclusion was checked by this review (see below). The author then concluded that the major dissociated complex contains only CO_3^{-2} ligand: this is correct. The stability of the dissociated complex increases with the total metal concentration: this is a direct experimental evidence that a polynuclear complex is formed. It is confirmed by the sensitivity analysis performed by the [89RIG] authors. This analysis was checked by this review (see below). Straightforward slope analysis (see below) showed that the dissociation equilibrium is

$$3\, NpO_2(CO_3)_3^{-4} \Leftrightarrow (NpO_2)_3(CO_3)_6^{-6} + 3\, CO_3^{-2}$$

The experimental data ($\log_{10}[CO_3^{-2}]$, $\log_{10}$(molar absorbance)) were graphically compared with theoretical curves calculated for constant total metal concentration, assuming that there was only one major soluble dissociated complex with different possible stoichiometry. This method allows the determination of the constant of the above equilibrium. In the same way

for M = Np or Pu $\quad 2\, UO_2(CO_3)_3^{-4} + MO_2(CO_3)_3^{-4} + \Leftrightarrow (UO_2)_2MO_2(CO_3)_6^{-6} + 3\, CO_3^{-2}$

mixed equilibria were studied in the same conditions by using the same experimental procedure. The corresponding equilibrium constants were determined by using the same graphical method. They were already accepted in the Uranium volume of this series of review [92GRE/FUG]. This review then accepts the same values for the mixed complexes (THIS HAS TO BE CHECKED WITH BILL for Pu).

This work also reports qualitative experimental observations useful to understand the methodology used, and when interpreting other publications on similar subject:

- The precipitation of $NpO_2CO_{3(s)}$ is slow: a few hours instead of a few seconds for the U and Pu analogues.
- Colour changes and spectrophotometric observation before and during the precipitation, suggest the formation of polymeric or colloidal species.

This review reproduced the graphical slope analysis as explained by the [89RIG] author. The results (table [89RIG]-1 and figure [89RIG]-1) confirm the interpretation of the author. This slope analysis is similar to the one performed by this review to test different interpretations of Maya's potentiometric titration in similar conditions (figure [84MAY]-6 in this appendix): in this previous [84MAY] work, not a unique interpretation could be proposed because (see the discussion on [84MAY] in this appendix) Maya did not use high enough carbonic gas partial pressure neither he varied the total Np(VI) concentration. Grenthe, Riglet et Vitorge choice of chemical conditions [86GRE/RIG, 89RIG] avoided this problem.

This review also checked sensitive analysis by trying to fit the data with other chemical species: this always gave very poor curve fitting results, and then confirmed the proposed original interpretation. In addition, this review calculated the equilibrium constant from each experimental data and looked for possible systematic deviation as a function of the key chemical parameters. For this sensitivity analysis, maximum weight was given to the data near the half reaction point where the theoretical error on the equilibrium constants is minimised. The weighted procedure practically eliminated the data corresponding to less than 25 % of one of the two complexes. It seems (figure [89RIG]-2) that the data at the lowest carbonic gas partial pressure could be shifted by up to 0.4 $\log_{10}$ unit toward higher stability of the dissociated complex; but this is still within uncertainty (table [89RIG]-2) of the corresponding series of measurements. In addition a few of the data at 1 atm are similarly shifted. The influence of $-\log_{10}[H^+]$ lead to the same observations (figure [89RIG]-2) and comments. In opposition no influence at all of the total metal concentration was observed. The fitted values of the molar absorbance coefficients have little influence on the $\log_{10}K$ value.

The above observations are consistent with the possible formation of minor species with a trinuclear hydroxo-carbonate complex. Such a species is indeed stable for U(VI) [92GRE/FUG]: it is $(UO_2)_3O(OH)_2HCO_3^+$. Spectrophotometric technique gives very reliable conclusion to determine the major species; but it is not much appropriate

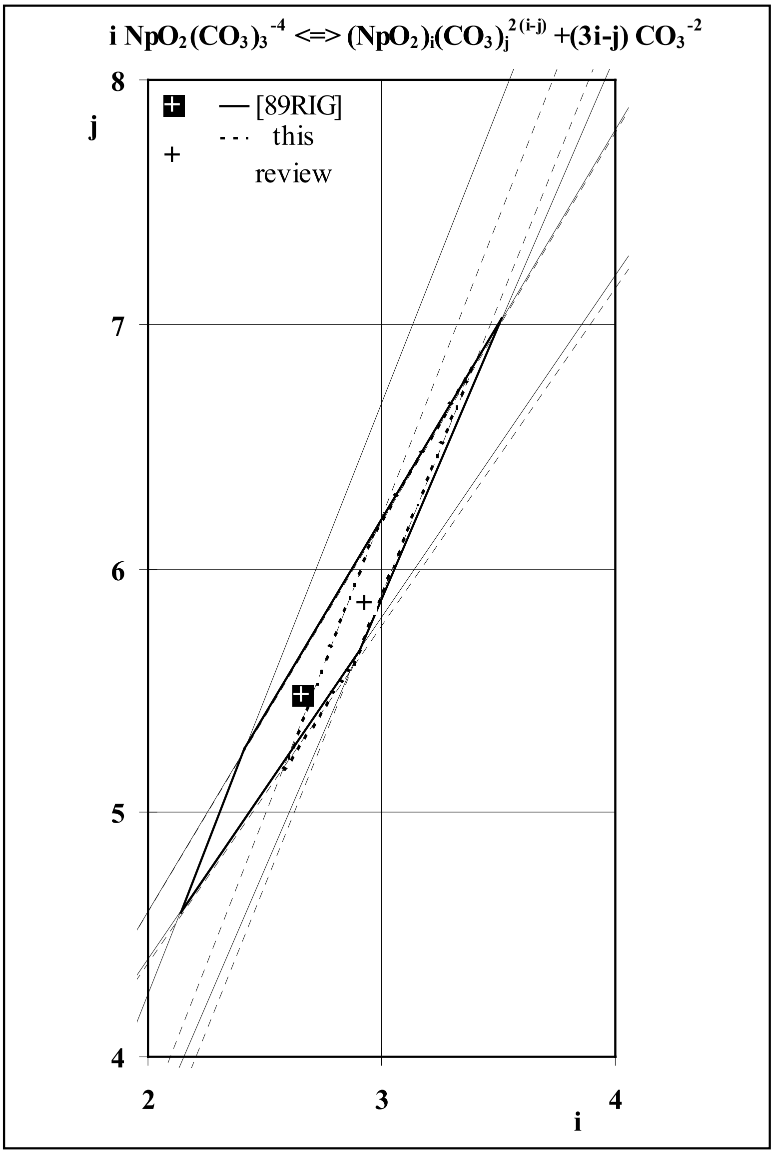


Figure [89RIG]-1 Result of the graphical determination of the stoichiometry of the soluble complex in equilibrium with the Np(VI) limiting complex in 1 to 10 mM Np(VI) aqueous bicarbonate solutions: the limiting complex is $NpO_2(CO_3)^{-4}$. The unknown dissociated complex is $(NpO_2)_i(CO_3)_i^{-2(i-j)}$. Absorbance measurements at 670 and 700 nm were plotted versus $\log_{10}[CO_3)^{-2}]$ for each $[Np(VI)]_{total}$. The slope of this type of curves at the half reaction point, and their shifts versus $\log_{10}[Np(VI)]_{total}$ were used to calculate two (theoretical linear) relationships involving the stoichiometric coefficients, i and j, as explained in the table [89RIG]-1. The stoichiometric coefficients are at the intercept of these two lines (crosses on the figure). The uncertainty on the graphical slope determinations corresponds to the thickness of each line, that is here represented by the domain between two lines (there are then 2x2=4 lines for the author determination, and also 4 (dashed) lines for this review reinterpretation at 670 nm) plotted with the a_i and b_i values of the table [89RIG]-1. The limit of the intersection of the domain is bolded: the possible stoichiometric coefficients are the i and j integer values falling inside this bolded domain. The [89RIG] original determination estimated graphically the slopes (p and P: table [89RIG]-1) and the corresponding uncertainty. This review used linear regressions and the corresponding 1.96 σ. The result of both determinations is the same: i=3, j=6, the dissociated complex is then $(NpO_2)_3(CO_3)_6^{-6}$.

to try to deduce quantitative data on minor species from only curve fitting. For this reason, this review did not try to check this type of interpretation.

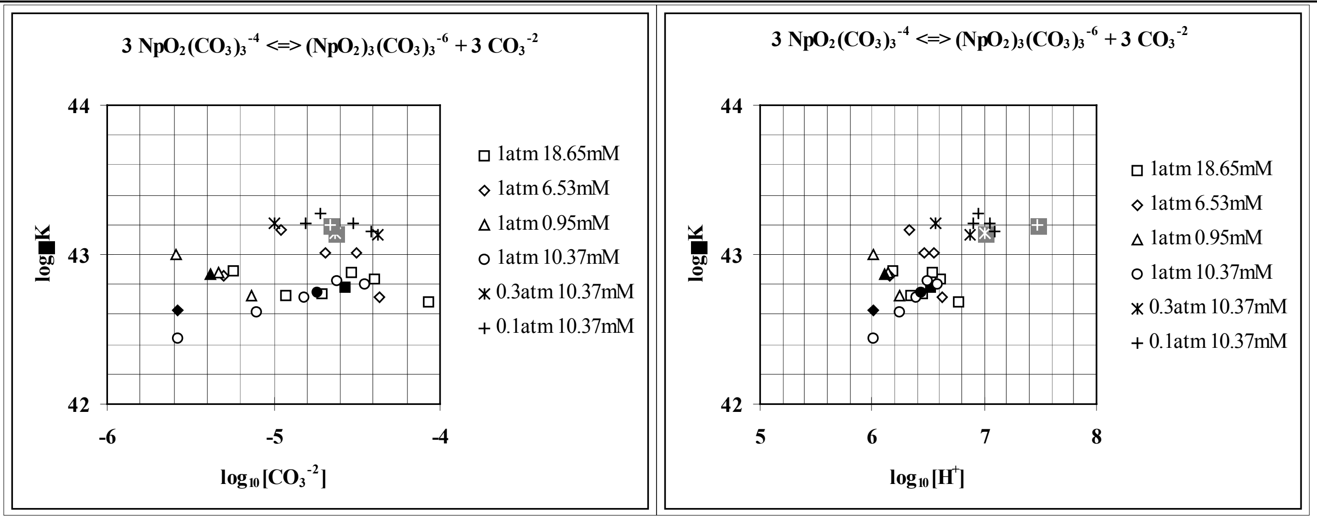
To determine the stoichiometry of the dissociated complex, the author used a wide range of chemical conditions. Now when this stoichiometry is established, one should keep only the best measurements or one should at least weight the data as a function of their theoretical error. This was automatically done by the author since she only used graphical determination. She proposed $\log_{10}K = 42.8 \pm 0.1$. This indeed corresponds exactly to the fitting result performed by this review from the best series of experimental data (highest P_{CO_2} and $[Np(VI)]_{total}$: $\log_{10}K = 42.79 \pm 0.19$. As already said the fitting results of the author series agree within uncertainty. The possible weighting procedures are quite arbitrary since many experimental sources of (un)accuracy could be taken into account, anyhow they all give very close results: typically $\log_{10}K = 42.88 \pm 0.27$ (table [89RIG]-2). So finally this review proposes

$\log_{10}K$ (I= 3M), = **42.79 ± 0.19 for $3\ NpO_2(CO_3)_3^{-4} + 6\ H^{+-} \Leftrightarrow (NpO_2)_3(CO_3)_3^{-6} + 3\ CO_{2(g)} + 3\ H_2O$**
$\log_{10}K$ (I= 1M) = 40.47 ± 2.95 calculated by this review from [84MAY]
then **$\log_{10}(\beta_{3,6,}/\beta_3)_{3M}$ = -10.06 ± 0.56** for $3\ NpO_2(CO_3)_3^{-4} \Leftrightarrow (NpO_2)_3(CO_3)_3^{-6} + 3\ CO_3^{-2}$
$\log_{10}(\beta_{3,6,}/\beta_3)_{1M}$ = -8.81 ± 1.07 calculated by this review from [84MAY]
then **$\log_{10}(\beta°_{3,6,}/\beta°_3)$ = -8.27 ± 1.23** and
$\Delta\varepsilon$ = 0.49 ± 0.49 $kg.mol^{-1}$
then **$\varepsilon(Na^+,(NpO_2)_3(CO_3)_6^{-6})$ = -0.75 ± 0.81 $kg.mol^{-1}$**, using $\varepsilon(Na^+,NpO_2(CO_3)_3^{-4}) = -0.49_4 \pm 0.21_3\ kg.mol^{-1}$ and $\varepsilon(H^+,ClO_4^-) = 0.14 \pm 0.02\ kg.mol^{-1}$.

The redox potential of the Np(VI)/Np(V) couple measured by Riglet [89RIG] in 0.1M Na_2CO_3 + 3M $NaClO_4$, is accepted by this review since the methodology used was first check on uranium corresponding system and gave reliable data consistent with those selected by the uranium review [92GRE/FUG]. It is also in good agreement with the previous value measured by Simakin [77SIM] and later determination by the same laboratory [95OFF/CAP]: these three works were used by this review to select the standard redox potential of the Np(VI)/Np(V) couple.

Table [89RIG]-2 Curve fitting results: The dissociation constant of the limiting complex, K = $[(NpO_2)_3(CO_3)_6^{-6}]\ P^3_{CO_2}$ / $([H^+]^6\ [NpO_2(CO_3)^{-4}]^3)$, was fitted from the different series of spectrophotometric data. Each series is one titration of Np(VI) at the initial Np(VI) total concentration and P_{CO_2} indicated in the first columns (at I = 3 M $NaClO_4$), the titration at 10.37 mM used 3 different P_{CO_2} values. The molar absorbance coefficients of the limiting and dissociated complexes, ε_L and ε_D respectively are also needed when the data at the corresponding wavelength (670 and/or 700 nm) are used for the fitting. Uncertainty is 1.96 standard deviation (when the corresponding data is fitted). The first lines are the results graphically measured by Riglet [89RIG]. All these fitting results are the same (within uncertainty), they are tabulated to discuss possible systematic deviation and then sensitivity analysis (figure [89RIG]-2). Bolded number could be proposed for the different reasons explained in the text, this review finally proposes 42.79 ± 0.19, which is also the value determined by the author with increased uncertainty.

	P_{CO_2} (atm)	$[Np]_t$ (mM)	$\varepsilon_{L,670nm}$ ($l.mol^{-1}.cm^{-1}$)	$\varepsilon_{D,670nm}$ / 3 ($l.mol^{-1}.cm^{-1}$)	$\varepsilon_{L,700nm}$ ($l.mol^{-1}.cm^{-1}$)	$\varepsilon_{D,700nm}$ / 3 ($l.mol^{-1}.cm^{-1}$)	$\log_{10}K$
[89RIG]	0.1 to 1	0.95to18.65	**20.8±0.2**	**4.8**±0.1			**42.8**±0.1
	1	18.65	20.83	4.99			42.786±0.201
	1	18.65	20.83±0.47	4.99	14.83±0.36	4.78	42.790±0.181
	1	6.53	20.83	4.99	14.83	4.78	42.924±0.457
	1	0.95	20.83	4.99	14.83	4.78	42.859±0.232
	0.1 to 1	10.37	20.83	4.99	14.83	4.78	43.013±0.441
	0.1 to 1	10.37	20.69±0.19	4.99	14.72±0.15	4.78	43.026±0.436
	0.1 to 1	0.95to18.65	20.83	4.99	14.83	4.78	42.921±0.338
series mean	0.1 to 1	0.95to18.65	20.83	4.99	14.83	4.78	42.867±0.324
	0.1 to 1	0.95to18.65	**20.774±0.218**		**14.788±0.167**		
	0.1 to 1	0.95to18.65	20.774	**5.038±0.238**	14.788	**4.854±0.331**	**42.921±0.341**
series mean	0.1 to 1	0.95to18.65	20.774	5.038	14.788	4.854	**42.883±0.265**
	1	18.65	20.78	5.038			**42.782±0.214**
	1	18.65	20.78	5.038	14.79	4.854	**42.790±0.193**
	1	6.53	20.78	5.038	14.79	4.854	42.921±0.467
	1	0.95	20.78	5.038	14.79	4.854	42.859±0.243
	0.1 to 1	10.37	20.78	5.038	14.79	4.854	43.015±0.439
	1	10.37	20.78	5.038	14.79	4.854	42.781±0.166
	0.3	10.37	20.78	5.038	14.79	4.854	43.145±0.108
	0.1	10.37	20.78	5.038	14.79	4.854	43.197±0.155



Figures [89RIG]-2 Sensitivity analysis on the determination of the limiting complex dissociation constant. Each series is one titration of Np(VI) at the initial Np(VI) total concentration and P_{CO_2} indicated on the figures (at I = 3 M $NaClO_4$), the 3 last series are the same titration. K = $[(NpO_2)_3(CO_3)_6^{-6}]\ P^3_{CO_2}$ / $([H^+]^6\ [NpO_2(CO_3)^{-4}]^3)$ is measured from the absorbance measurement at 670 nm. Bold point represents the $\log_{10}K$ weighted mean of the corresponding series, plotted at $\log_{10}[CO_3^{-2}]$ (or $\log_{10}[H^+]$) corresponding to the best precision (i.e. at the half reaction point). Uncertainty on the mean of each series (table [89RIG]-2) is between 0.15 and 0.47 unit $\log_{10}$. The value selected by this review is $\log_{10}K$ = 42.79 ± 0.19 which is consistent with 42.8 ± graphically determined by Riglet [89RIG].

[90RIG]

Chantal Riglet CEA-R-5535.

It is [89RIG]

[90CAP/VIT]

Capdevila H., Vitorge P. *Temperature and Ionic Strength Influences on U(VI/V) and U(IV/III) Redox Potentials in Aqueous Acidic and Carbonate Solutions*. Actinides 89 Tashkent, (September 24-29, 1989) J. Radioanal. and Nuclear Chem., Articles, 143,2, 403-14 (1990)

[90PRA/MOR]

Pratopo I., Moriyama H., Higashi K. *Carbonate complexation of neptunium(IV) and analogous complexation of ground-water uranium.* Radiochim. Acta 51 (1990) 27-31

[91PRA/YAM]

Pratopo, M.I., Yamaguchi, T., Moriyama, H., Higashi, K. *Adsorption of Np(IV) on Quartz in Carbonate Solutions,* Radiochim. Acta, 55, 209 (1991).

[92CAP]

Capdevila H. *Données thermodynamiques sur l'oxydoréduction du plutonium en milieux acide et carbonate. Stabilité de Pu(V)*. Thesis Paris-sud (Paris 11) Université Orsay centre (5 June 1992). CEA-R-5643 (1993).

[93CAP]

CEA-R-5643 (1993). See [92CAP]

[93GIF/VIT]

Giffaut E., Vitorge P., Capdevila H. *Corrections de température sur les coefficients d'activité calculés selon la TIS*. CEA-N-2737 (1993) see [94GIF/VIT]

[93LI/KAT]

Li Y., Kato Y., Yoshida Z. *Electrolytic preparation of neptunium species in concentrated carbonated media*. Radiochim. Acta 60 (1993) 115-119.

Concerning Np(VI), this publication presents coulometric preparation of Np(VI) from Np(V), and of Np(V) from Np(VI) in 1 M $HClO_4$ and in 1 M Na_2CO_3 aqueous solution. The

$$NpO_2^{+2} + e^- \Leftrightarrow NpO_2^+$$

reaction is found to be reversible. The normal potential of the corresponding equilibrium is found to be

$$E_{Np(VI)/Np(V)\text{ in 1M }HClO_4} = 0.93\text{ V/SSE}$$

The potential of the SSE reference electrode, 0.24 ± 0.01 V was measured at 23 ± 2°C. So

$$E_{Np(VI)/Np(V)\text{ in 1M }HClO_4} = 1.07\text{ V/SHE}$$

which is not consistent with the data selected by this review (TO BE CHECKED BY HEINO). In the same way

$$E_{Np(VI)/Np(V)\text{ in 1M }Na_2CO_3} = 0.25\text{ V/SSE}$$

and

$$E_{Np(VI)/Np(V)\text{ in 1M }Na_2CO_3} = 0.49\text{ V/SHE}$$

The Np(VI)/Np(V) potential shift from acidic to these carbonate media is

$$E_{Np(VI)/Np(V)\text{ in 1M }Na_2CO_3} - E_{Np(VI)/Np(V)\text{ in 1M }HClO_4} = 0.68\text{V}$$

according to the authors. This corresponds to

$$\log_{10}(\beta_{3Np(VI)}/\beta_{3Np(V)})_{0.2\text{ to 3 M }K_2CO_3} = 11.5$$

since it is known that the two limiting complexes are $NpO_2(CO_3)_3^{4-}$ and $NpO_2(CO_3)_3^{5-}$. Similar values were reported previously: 0.71 ± 0.014 V [74SIM] which corresponds to 11.2 ± 0.9 shift on $\log_{10}\beta_3$. No indication is given on junction potential and on the uncertainty, so this review disregarded the result of this [93LI/KAT] work. Still it agres with Simakin's work [77SIM] selected by this review.

[93PRA]

Pratopo, M.I., *Basic study on geochemical behaviour of neptunium*, Thesis Kyoto University (1993)

This thesis has also been published as [89PRA/MOR2, 89PRA/MOR1, 90PRA/MOR, 93PRA/MOR1, 91PRA/YAM, 93PRA/MOR2].

[93PRA/MOR1]

Pratopo, M.I., Moriyama, H., Higashi, K. *Carbonate complexation of Np(VI) in near-neutral solutions*, J. Nucl. Sci. Tech., 30(10) (1993) 1024-1029.

This work is similar to the [95MOR/PRA] later one published by the same authors. It is also part of [93PRA] Prapoto's thesis. $^{237}Np(VI)$ solubility was measured in aqueous solutions prepared by adding to 6 ml of a 0.1 M $NaClO_4$ solution some $NaHCO_3$ to provide total carbonate concentration 25.3 to 167 mM. It is not clear whether the $NaHCO_3$ used for addition was the solid phase or a concentrated solution. In both cases this procedure should not allow an accurate knowledge of volumetric concentrations, specially for $[Na^+]$. The total carbonate concentration is at least of the same order of magnitude than the $NaClO_4$ concentration. The ionic medium was then not constant within the series of solubility measurements, specially $[Na^+]$ varied from 0.15 to 0.43 M (at least -see below- as calculated by this review), which is indeed more than 0.1 M $NaClO_4$. pH measurement reported by the authors (9.61 to 10.5) is, in some samples, quite higher than the theoretical value calculated assuming the above procedure. The authors then probably also added another product (possibly NaOH) to vary the pH. It is not possible to calculate the amount of (possibly) added NaOH for pH adjustment, with a good accuracy, since equilibration with the air during this pH adjustment also adds acidic reactant (carbonic gas). $[Na^+]$ cannot then be estimated with a good accuracy. For this reason, ionic strength corrections on the carbonic acid equilibrium constants cannot be calculated with good accuracy (and the one used by the authors are then probably in error).

The authors reported the absorption spectrum of the most concentrated (in Np(VI) and total carbonate), less basic solution. Its quality is not very good when comparing with the previously published spectra [81WES/SUL, 86GRE/RIG] cited by the authors. Still it corresponds to the spectrum of the pure limiting complex, $NpO_2(CO_3)_3^{-4}$ in opposition with what the authors said. The authors plotted their experimental solubility data as a function $\log_{10}[CO_3^{-2}]$, and proposed a

Table [95OFF/CAP]-1: Redox potential of the Np(VI)/Np(V) couple measured in Na_2CO_3 aqueous solutions. The original data were measured versus an Ag/AgCl reference electrode. This review recalculated the Np(VI)/Np(V) potential values vs. SHE. They are consistent with Offerlé's values [95OFF/CAP]. N data were measured in each condition (t (°C): first column, [Na_2CO_3]: first line), their mean and 1.96 σ are here tabulated. The corresponding overall uncertainty (1.96 $(\Sigma/(N-p))^{0.5}$ where N is the total number of data, p is the number of experimental conditions, and Σ is the least square sum) is 4.6 mV for the 105 measurements (N-p = 64), and is also calculated (first line) for each series (same [Na_2CO_3]).

t	0.22M(2.8mV)	N	0.55(3.4mV)	N	1(2.6mV)	N	1.25(6mV)	N	1.5(4.4mV)	N	2(6.5mV)	N
5	0.4646±0	2	0.5000±0.0042	2	0.5338±0.0014	2	0.5388±0.0014	2	0.5397±0.0023	3	0.5607	1
15	0.4521±0.0014	2	0.4822±0.0028	2	0.5164±0.0028	2	0.5219±0.0028	2	0.5217±0.0042	2	0.5403±0.0042	2
25	0.4344±0.0041	5	0.4671±0.0010	4	0.5002±0.0024	6	0.5003±0.0090	5	0.4980±0.0055	5	0.5071±0.0095	6
35	0.4176±0	2	0.4513±0.0014	2	0.4834±0.0042	2	0.4703±0.0042	2	0.4790±0.0063	3	0.4838±0.0014	2
45	0.4005±0.0020	3	0.4310±0.0042	2	0.4613±0.0028	2	0.4530±0.0028	2	0.4558±0.0042	2	0.4659±0.0019	4
55	0.3812±0.0014	2	0.4102±0.0069	2	0.4432±0.0028	2	0.4458±0.0028	2	0.4383±0.0011	3	0.4494±0.0042	2
60					0.4339±0.0014	2	0.4360±0	2	0.4301±0	2	0.4385±0.0014	2
10											0.5423	1

Table [95OFF/CAP]-2: Extrapolations to zero ionic strength of the Np(VI)/Np(V) redox potential from data measured in Na_2CO_3 aqueous solutions. $\Delta\varepsilon = \varepsilon(NpO_2(CO_3)_3^{-4},Na^+) - \varepsilon(NpO_2(CO_3)_3^{-5},Na^+)$. The results of unweighted SIT regressions from the data of the table [95OFF/CAP]-1 are italicised to stress, that it should be weighted by using the accuracy at each Na_2CO_3 concentration. It is equivalent to use all the original data at each temperature: the results of these SIT regressions (using all the data) are here tabulated. The values calculated by Offerlé are in the columns [95OFF/CAP]. At each temperature, the Debye-Hückel term, was calculated with A, B and a_j parameters (appendix B) where a_j was assumed to be independent of the temperature. It is calculated (table [95OFF/CAP]-6) with the approximation 1.5 = B a_j at 25°C.

t (°C)		Δε (kg.mol^{-1})	[95OFF/CAP]		E'° (V/SHE)	[95OFF/CAP]
5	*0.263±0.089*	0.266±0.063	0.296	*0.3749±0.0124*	0.3744±0.0163	0.3749
15	*0.217±0.078*	0.217±0.050	0.238	*0.3568±0.0112*	0.3568±0.0142	0.3583
25	*0.128±0.106*	0.121±0.043	0.155	*0.3405±0.0158*	0.3416±0.0131	0.3411
35	*0.079±0.107*	0.079±0.065	0.113	*0.3201±0.0165*	0.3201±0.0199	0.3195
45	*0.064±0.083*	0.065±0.039	0.100	*0.2957±0.0132*	0.2948±0.0131	0.2942
55	*0.075±0.091*	0.071±0.056	0.106	*0.2704±0.0149*	0.2705±0.0183	0.269
60	*-0.071±0.088*	-0.071±0.051	-0.030	*0.2876±0.0176*	0.2876±0.0200	0.285
25(a)	*0.1270.096*		0.178	*0.3402±0.0142*		

(a)The last line used the results of t polynomial regression (to the second degree) about 25°C (table [95OFF/CAP]-5).

Table [95OFF/CAP]-3: Variation of the Δε coefficient with the temperature for the Np(VI)/Np(V) redox couple in Na_2CO_3 aqueous solutions. Second order polynomial regressions (or linear regression(a)) are performed from the data of the table [95OFF/CAP]-2 as a function of (t-25). This produces Δε at 25°C, the first order term (that is also Δε derivative as a function of t) Δε', and (eventually) the second order term Δε" / 2. The bolded proposed values are the results of the second degree polynomial regression excluding the measurement at 60°C. The values calculated by Offerlé are in the last line [95OFF/CAP].

	Δε (kg.mol^{-1})				Δε' (g.mol^{-1}.K^{-1})				Δε" / 2 (g.mol^{-1}.K^{-2})	
5 to 55°C(a)	*0.131*	*± 0.027*	*0.158(b*	*± 0.029*	-5.17		*-4.13(b)*	*± 0.84*	*0.104*	
5 to 55°C	**0.129**	**± 0.026**	0.158(b)	± 0.030	**-5.28**	**± 1.00**	-4.21(b)	±±0.86	**0.107**	**± 0.057**
5 to 60°C(a)	*0.150*	*± 0.077*	*0.154(b)*	*± 0.018*	-5.22		*-5.00(b)*	*± 0.86*	*0.013*	
5 to 60°C	0.148	± 0.076	0.154(b)	± 0.018	-5.33	± 2.65	-5.04(b)	± 0.85	0.018	± 0.119
[95OFF/CAP]	0.15	± 0.05			-5	± 0.1			0.02	

(a) The mean value (and not all the E measurements) of the Np(VI)/Np(V) redox potential measured in each experimental condition ([Na_2CO_3], t) were extrapolated to zero ionic strength (producing Δε(T)).

(b) linear regression (Δε" = 0).

slope analysis. In opposition with what the authors said, this review found that the [CO_3^{-2}] domain of experimental conditions is too small in comparison to the scattering of the experimental results, to imagine to obtain any conclusion from such analysis, and from such data. Besides the observed scattering of the solubility data, as said above the chemical conditions ([CO_3^{-2}], [Na^+] and pH) are known with poor accuracy. In addition to this poor experimental methodology and interpretation, the authors did not recognise (as said above) that there was a unique predominating soluble species all over their measurements: the limiting complex, $NpO_2(CO_3)_3^{-4}$.

This last statement is confirmed by the absorbance measurements reported by the authors. As for the solubility measurement they proposed a slope analysis. And again this review did not detect any change (more than the relatively important scattering of the reported measurements) in the absorbance in the different chemical conditions. In addition, slope analysis strongly relies on the molar absorbance coefficients of the pure species, in the case of spectrophotometric measurement. Neither these coefficients are proposed by the authors, nor they can be deduced (since there is no evidence of the second species).

So the starting complex, the number of OH ligand exchanged and the final complexes proposed by the authors are completely in error

The experimental data reported by the authors can be explained by the well-known chemical species of Actinides(VI) in bicarbonate / carbonate aqueous solutions: in opposition with what the authors said, there is no

Table [95OFF/CAP]-4: Proposed Δ_rH, Δ_rS and Δ_rCp at 25°C for the Np(VI)⇒Np(V) redox reaction deduced from potential measurements as a function of temperature in Na_2CO_3 aqueous solutions. The values calculated by Offerlé are in the lines [95OFF/CAP].

	[Na2CO3] (M)	E (V/SHE)	lgK	Δ_rG (kJ.mol.$^{-1}$)	Δ_rH(kJ.mol.$^{-1}$)	Δ_rS(J.mol.$^{-1}$K^{-1})	Δ_rCp(J.mol.$^{-1}$K^{-1})
	0	$0.340_3 \pm 0.002_3$	$5.75_1 \pm 0.03_9$	$-32.8_3 \pm 0.2_2$	$-88._{77} \pm 2._{93}$	$-187._6 \pm 9._7$	-759 ± 141
[95OFF/CAP]	0	$0.336_2 \pm 0.009_4$				-190 ± 5	-345 ± 750
	0.22	$0.434_8 \pm 0.002_7$	$7.35_0 \pm 0.04_5$	$-41.9_5 \pm 0.2_6$	$-88._{73} \pm 0._{91}$	$-156._9 \pm 3._0$	-304 ± 86
[95OFF/CAP]	0.22					-159	-305
	0.55	$0.467_4 \pm 0.003_3$	$7.90_0 \pm 0.05_6$	$-45.0_9 \pm 0.3_2$	$-94._{16} \pm 1._{18}$	$-164._6 \pm 3._9$	-352 ± 112
[95OFF/CAP]	0.55					-164	-355
	1	$0.500_1 \pm 0.002_7$	$8.45_4 \pm 0.04_6$	$-48.2_5 \pm 0.2_6$	$-99._{06} \pm 0._{93}$	$-170._4 \pm 3._1$	-282 ± 87
[95OFF/CAP]	1	0.504_5				-169	-235
	1.25	$0.497_1 \pm 0.010_1$	$8.40_2 \pm 0.17_1$	$-47.9_6 \pm 0.9_8$	$-108._{42} \pm 2._{81}$	$-202._8 \pm 9._4$	475 ± 329
[95OFF/CAP]	1.25					-200	515
	1.5	$0.498_6 \pm 0.004_5$	$8.42_8 \pm 0.07_6$	$-48.1_1 \pm 0.4_4$	$-107._{53} \pm 1._{00}$	$-199._3 \pm 3._3$	64 ± 124
[95OFF/CAP]	1.5					-197	128
	2	$0.507_9 \pm 0.007_6$	$8.58_6 \pm 0.12_9$	$-49.0_1 \pm 0.7_4$	$-118._{71} \pm 2._{48}$	$-233._8 \pm 8._3$	891 ± 262
[95OFF/CAP]	2					-230	758

Table [95OFF/CAP]-5: **Physical parameters used to extrapolate E, Δ_rH, Δ_rS and Δ_rCp to 0 ionic strength at different temperatures**. D([Na_2CO_3]) is the Debye-Hückel term calculated in 0.22, 0.55, 1, 1.25, 1.5 and 2 M Na_2CO_3 solutions corresponding to the ionic strength 0.661, 1.655, 3.021, 3.789, 4.563, and 6.121 mol.kg^{-1} respectively. A and Ba_j are from the appendix B. D' and D" are first and second order derivatives as a function of temperature, at 25°C, numerically calculated from D values at 20, 25 and 30°C. T° = 298.15 K.

t	RTln10/F	A	Ba_j	D(0.22)	D(0.55)	D(1)	D(1.25)	D(1.5)	D(2)
0	0.054199	0.4913	1.4836	0.1811	0.2173	0.2386	0.2460	0.2517	0.2603
5	0.055191	0.4943	1.4867	0.1819	0.2183	0.2397	0.2471	0.2529	0.2614
10	0.056183	0.4976	1.4899	0.1829	0.2195	0.2409	0.2483	0.2541	0.2627
15	0.057175	0.5012	1.4931	0.1840	0.2207	0.2423	0.2497	0.2556	0.2642
20	0.058168	0.5050	1.4968	0.1852	0.2221	0.2437	0.2512	0.2570	0.2656
25	0.05916	0.5091	1.5000	0.1865	0.2235	0.2453	0.2528	0.2587	0.2674
30	0.060152	0.5135	1.5037	0.1878	0.2251	0.2470	0.2545	0.2604	0.2692
35	0.061144	0.5182	1.5073	0.1893	0.2268	0.2488	0.2564	0.2623	0.2711
40	0.062136	0.5231	1.5110	0.1908	0.2286	0.2507	0.2584	0.2643	0.2731
45	0.063128	0.5282	1.5151	0.1924	0.2304	0.2527	0.2603	0.2663	0.2752
50	0.06412	0.5336	1.5192	0.1941	0.2323	0.2548	0.2625	0.2685	0.2774
55	0.065112	0.5392	1.5233	0.1958	0.2344	0.2569	0.2647	0.2708	0.2797
60	0.066104	0.5450	1.5274	0.1976	0.2365	0.2592	0.2670	0.2731	0.2821
65	0.067097	0.5511	1.5315	0.1996	0.2387	0.2616	0.2694	0.2756	0.2847
70	0.068089	0.5573	1.5361	0.2015	0.2409	0.2639	0.2719	0.2781	0.2872
75	0.069081	0.5639	1.5402	0.2036	0.2433	0.2665	0.2745	0.2808	0.2900
100	0.074041	0.6000	1.5635	0.2148	0.2563	0.2805	0.2888	0.2953	0.3049
25			T° D'	0.078884	0.091232	0.097970	0.100207	0.101919	0.104434
25			T°² D"	0.267985	0.292568	0.302677	0.305426	0.307308	0.309698

contradiction with the literature cited by them. To confirm this, this review plotted these data with later works by the same authors [95MOR/PRA] with exactly the same methodology and with others [97VIT/CAP]: see the corresponding discussion in this appendix.

The interpretation of this publication is straightforward: the authors only had the pure limiting complex, $NpO_2(CO_3)_3^{-4}$. This corresponds to the predicted speciation calculated with the equilibrium constants selected by this review; and this also corresponds to the spectrophotometric data presented by the authors (despite what they say). Their solubility measurements are probably out of equilibrium. Since the experimental data are found to be very scattered in comparison to previous published works using the same techniques on the same chemical system, and since the chemical conditions are not known with reasonable accuracy, this review did neither considered the interpretation proposed by the authors, nor tried to reinterpret the data. The expected solubility equilibrium is

$$Na_4NpO_2(CO_3)_{3(s)} \Leftrightarrow NpO_2(CO_3)_3^{4-} + 4\ Na^+$$

As explained above there is a huge systematic uncertainty on [Na^+]: it is even more important on [Na^+]^4.

[93PRA/MOR2]

Pratopo, M.I., Moriyama, H., Higashi, K. Sorption and Colloidal Behaviour of Np(IV) in a Bentonite-Carbonate Solution System, J. Nucl. Sci. Tech., 6 (1993) 560.

[94GIF/VIT]

Giffaut E., Vitorge P., Capdevila H. *Adjustment of Activity Coefficients as a Function of Changes in Temperature, using the Specific Interaction Theory*. Actinides-93, Santa Fe, September 19-24 (1993). J. Alloys Compounds 213/214, 278-285 (1994)

Table [95OFF/CAP]-6: Results of extrapolation to zero ionic strength for E, Δ_rH, Δ_rS and Δ_rCp that were obtained at 25°C by polynomial regression of the Np(VI)/Np(V) redox potential from data measured in Na_2CO_3 aqueous solutions. The italicised values are extrapolation to zero ionic strength of the table [95OFF/CAP]-4 data. The values calculated from the interpretation of this [95OFF/CAP] publication proposed by this review are in the column "expected values", they are extracted from the tables [95OFF/CAP]-3 and 4. The aim of this table is to show that the different ways to perform extrapolation to zero ionic strength by using the SIT and the approximations explained in the text (neglecting third order terms) are consistent: they lead to the same results within uncertainty. The notations ' and " mean first and second order derivatives as a function of temperature. The values calculated by Offerlé are in the column [95OFF/CAP].

Extrapolation to I = 0 of	*E / 0.05916 data*			expected values			[95OFF/CAP]		
E°(V/SHE) / 0.05916	5.75_3	±	0.24_8	5.75_1	±	0.03_9			
E°(V/SHE)	0.340	±	0.015	0.340_3	±	0.002_3	0.341	±	0.017
Δε(kg.mol^{-1})	0.12_7	±	0.09_8	0.12_9	±	0.02_6	0.15	±	0.05
Extrapolation to I = 0 of	*Δ_rH / (R T° ln10) data*			expected values			[95OFF/CAP]		
$\Delta_rH°$(kJ.mol^{-1}) / (R T° ln10)	-15.6_1	±	0.6_3	-15.5_5	±	0.5_1			
T° Δε'(kg.mol^{-1})	*-1.475*	±	*0.248*	-1.575	±	0.009			
$\Delta_rH°$(kJ.mol^{-1})	$-89._1$	±	$3._6$	$-88._8$	±	$2._9$			
Δε'(g.mol^{-1}K^{-1})	-4.94_9	±	0.83_2	-5.28_1	±	0.03_0	-5	±	1
Extrapolation to I = 0 of	*Δ_rS / (R ln10) data*			expected values			[95OFF/CAP]		
$\Delta_rS°$(J.mol^{-1}K^{-1}) / (R ln10)	-9.8_5	±	0.7_2	-9.8_0	±	0.5_1			
T°De'+de(kg.mol^{-1})	*-1.35*	±	*0.29*	-1.45	±	0.03			
Δε'(g.mol^{-1}K^{-1})	-4.94_9	±	0.83_2	-5.28_1	±	0.03_0			
$\Delta_rS°$(J.mol^{-1}K^{-1})	$-188._6$	±	$13._8$	$-187._6$	±	$9._8$	-190	±	5
Extrapolation to I = 0 of	*Δ_rCp / (R ln10) data*			expected values			[95OFF/CAP]		
$\Delta_rCp°$(J.mol^{-1}K^{-1}) / (R ln10)	*-37*	±	*25*	-40					
2T°Δε'+T°²Δε"(kg.mol^{-1})	*17*	±	*10*	16					
T°²Δε"(kg.mol^{-1})	$19._8$	±	$10._1$	$19._1$					
$\Delta_rCp°$(J.mol^{-1}K^{-1})	-716	±	486	-759			-345	±	750
Δε"(g.mol^{-1}K^{-2})	0.22_3	±	0.03_6	0.21_5			0.04		

[95MOR/PRA]

Moriyama, H., Pratopo, M.I., Higashi, K. *Hydrolysis and carbonate complexation of Np(VI)*, Radiochim. Acta, 69 (1995) 49-54.

See the comments in the appendix, on [93PRA/MOR] and [97VIT/CAP]

[95OFF/CAP]

Offerlé S., Capdevila H., Vitorge P. *Np(VI)/Np(V) en milieu carbonate concentré* (in French) CEA-N-2785 (1995)

This is the publication as an open report, of Offerlé's pre-thesis short experimental work (four months). The original experimental results were tabulated together with some remarks of the responsible of the stage, that were taken into account by this review. The redox potential of the Np(VI)/Np(V) couple was measured in 0.22 to 2 M Na_2CO_3 aqueous solutions at 5 to 60°C, versus an Ag/AgCl reference electrode, using cyclic voltametry technique on typically 0.6 mM Np(V) solution. For each Na_2CO_3 concentration, a new working solution and a new reference electrode was prepared. Temperature was changed up or down before a measurement, during typically one day, so there were usually several measurements in each experimental condition ([Na_2CO_3], t) corresponding to an increase and decrease of temperature. The reference electrode was checked twice daily. A remark in the original publication [95OFF/CAP] said that it was not clear whether only the stability of the electrode was hence checked, or whether its junction potential was also measured. A later publication [97VIT/CAP] gave indications that lead this review to assume that values (less than 1 mV) tabulated in the original publication [95OFF/CAP] were junction potential measurements. The pick intensity was proportional to the scanning speed, the potential shift between the oxidation and reduction picks was a little more than the theoretical value, but its mean value, $E_{1/2}$, remained independent of the scanning speed. This confirms that, as for other reversible and quasi-reversible systems studied in this laboratory [87RIG/VIT, 87ROB, 89RIG, 89RIG/ROB, 92CAP, 95CAP/VIT, 90CAP/VIT], $E_{1/2}$, is a good approximation of the thermodynamic potential of the studied redox equilibrium. For the treatment of the data, it was assumed that the potential was controlled by the

$$NpO_2(CO_3)_3^{-5} \Leftrightarrow NpO_2(CO_3)_3^{-4} + e^-$$

redox equilibrium. Corrections for the dissociation of the Np(V) limiting complex, were calculated to be only 5.7 mV for the less concentrated solutions at 25°C (Table [95OFF/CAP]-4), which is still more than the uncertainty (Table [95OFF/CAP]-1). Extrapolation to zero ionic strength was performed at each temperature by using the SIT with the same procedure and physical parameters as recommended by this review. A local approximation (second order polynomial regression about 25°C) was used for the treatment of the data as a function of temperature: first order term is related to mean entropy, and second order one to mean heat capacity changes corresponding to the above equilibrium. Similar treatment was performed for specific interaction coefficients. E° was hence determined. The numerical values of thermodynamic parameters ($\Delta_rS°$, $\Delta_rCp°$), Δε° and its first and second derivatives as a function of T, were finally found to be similar to those selected for Uranium [92GRE/FUG] or published for Uranium and Plutonium by one of the authors [92CAP]. All this seems reliable and correct. This review checked all the calculation and found similar numbers.

Recalculations performed by this review are now explained. The original data (V/SSE) were recalculated (V/SHE) taking into account the (small) errors pointed out by Vitorge [95OFF/CAP] and Capdevila [96OFF/VIT]. In each experimental condition the E mean value and its uncertainty were calculated as indicated in the table [95OFF/CAP]-1. The

Table [95OFF/CAP]-7 Influence of the dissociation of the Np(V) limiting carbonate complex, on the normal potential of the Np(VI)Np(V) couple at 25°C, ΔE, calculated with the data selected by this review, in Na_2CO_3 or (last data) $NaClO_4$ aqueous solution. The results of extrapolation to zero ionic strength (bottom part of the table) using the works [77SIM, 89RIG, 95OFF/CAP] selected (and as interpreted) by this review, and taking into account this correction, are bolded. When nothing else is stated, data are from Na^+ aqueous solutions.

$[CO_3^{-2}]$	$[Na^+]$	ΔE(V)	$[CO_3^{-2}]$	$[Na^+]$	ΔE(V)	$[CO_3^{-2}]$	$[Na^+]$	ΔE(V)
0.1000	0.2	0.0242	0.3055	0.6110	0.0028	0.7762	1.5525	0.0003
0.1318	0.2637	0.0155	0.5000	1	0.0009	1.0000	2	0.0002
0.1928	0.3855	0.0075	0.5070	1.0140	0.0009	1.0116	2.0232	0.0001
0.2042	0.4083	0.0067	0.5500	1.1	0.0007	1.0186	2.0372	0.0001
0.2200	0.44	0.0057	0.7379	1.4758	0.0003	1.2500	2.5	0.0001
0.2500	0.5	0.0044	0.7500	1.5	0.0003	0.1	3	0.0007

E(V/SHE) is the normal potential of the Np(VI)Np(V) couple at 25°C in Na_2CO_3 (or $NaClO_4$ [89RIG]) media, E_c is its value corrected for the dissociation of $NpO_2(CO_3)_3^{-5}$.

$mol.l^{-1}$	E	Ec	$mol.l^{-1}$	E	Ec	$mol.l^{-1}$	E	Ec	$mol.l^{-1}$	E	Ec
[89RIG]			[95OFF/CAP]			1	0.5009	0.5007	1.5	0.4940	0.4939
3	0.496	0.4953	0.22	0.4370	0.4312	1	0.5019	0.5017	1.5	0.4960	0.4959
[77SIM]			0.22	0.4320	0.4262	1	0.4989	0.4987	1.5	0.5000	0.4999
0.1318	0.4369	0.4214	0.22	0.4340	0.4282	1	0.5009	0.5007	1.5	0.5000	0.4999
0.2042	0.4465	0.4398	0.22	0.4330	0.4272	1	0.4989	0.4987	2	0.5146	0.5146
0.3055	0.4583	0.4555	0.22	0.4360	0.4302	1.25	0.5061	0.5060	2	0.5026	0.5026
0.5070	0.4664	0.4655	0.55	0.4320	0.4313	1.25	0.5021	0.5020	2	0.5056	0.5056
0.7379	0.4752	0.4748	0.55	0.4340	0.4333	1.25	0.4961	0.4960	2	0.5086	0.5086
1.0186	0.4923	0.4922	0.55	0.4330	0.4323	1.25	0.4951	0.4950	2	0.5016	0.5016
1.5311	0.4994	0.4993	0.55	0.4360	0.4353	1.25	0.5021	0.5020	2	0.5096	0.5096
2.0893	0.5105	0.5105	1	0.4999	0.4997	1.5	0.5000	0.4999			

Results of SIT regressions.

$\Delta\varepsilon(kg.mol^{-1})$	E°(V/SHE)	$\log_{10}\beta_3^{(VI)\circ}$	ΔE°(V/SHE)	ΔE° F/RT	
$-0.04_7 \pm 0.05_1$	$0.340_4 \pm 0.009_3$	$19.31_7 \pm 0.29_5$	$0.818_6 \pm 0.010_1$	$13.83_7 \pm 0.17_1$	[a][77SIM]K_2CO_3
$-0.02_6 \pm 0.04_2$	$0.335_2 \pm 0.007_7$	$19.40_5 \pm 0.28_1$	$0.823_8 \pm 0.008_7$	$13.92_5 \pm 0.14_7$	[b][77SIM]K_2CO_3
$0.12_0 \pm 0.04_3$	$0.341_8 \pm 0.005_4$	$19.29_4 \pm 0.26_6$	$0.817_2 \pm 0.006_7$	$13.81_4 \pm 0.11_4$	[77SIM]
$0.08_1 \pm 0.02_5$	$0.348_9 \pm 0.003_1$	$19.17_3 \pm 0.25_5$	$0.810_1 \pm 0.005_1$	$13.69_3 \pm 0.08_6$	[a][77SIM]
$0.14_2 \pm 0.04_9$	$0.337_7 \pm 0.004_5$	$19.36_2 \pm 0.28_0$	$0.821_3 \pm 0.008_5$	$13.88_2 \pm 0.14_4$	[95OFF/CAP]
$0.12_1 \pm 0.04_3$	$0.341_6 \pm 0.006_7$	$19.29_7 \pm 0.27_4$	$0.817_4 \pm 0.007_8$	$13.81_7 \pm 0.13_2$	[a][95OFF/CAP]
$0.05_3 \pm 0.04_8$	$0.354_0 \pm 0.008_1$	$19.08_7 \pm 0.28_4$	$0.805_0 \pm 0.009_0$	$13.60_7 \pm 0.15_3$	[c][95OFF/CAP]
$0.05_0 \pm 0.04_8$	$0.354_7 \pm 0.008_0$	$19.07_6 \pm 0.28_3$	$0.804_3 \pm 0.008_9$	$13.59_6 \pm 0.15_1$	[a,c][95OFF/CAP]
$0.13_3 \pm 0.03_7$	**$0.339_1 \pm 0.005_6$**	**$19.33_9 \pm 0.26_7$**	**$0.819_9 \pm 0.006_9$**	**$13.85{=} \pm 0.11_6$**	**[77SIM, 89RIG 95OFF/CAP]**
$0.10_7 \pm 0.03_3$	$0.344_0 \pm 0.005_0$	$19.25_6 \pm 0.26_3$	$0.815_0 \pm 0.006_4$	$13.77_6 \pm 0.10_8$	[a][77SIM, 89RIG 95OFF/CAP]

[a]Without correction for $NpO_2(CO_3)_3^{-5}$ dissociation. [b]With (Na^+ and not K^+) correction for $NpO_2(CO_3)_3^{-5}$ dissociation. [c]excluding data in less concentrated CO_3^{-2} solutions (0.22M Na_2CO_3).

overall (measurements during 17 days, involving 6 series of solution and reference electrodes) mean accuracy was found to be 4.6 mV. The accuracy of a given series of solutions (same $[Na_2CO_3]$) range between 2.6 to 6.5 mV which is more than the measured junction potential (± 0.6 to 1.2 mV) which were then neglected by this review. Either all the data E(T,I), or their mean in each experimental condition was then extrapolated to zero ionic strength. Both procedures gave similar E(T,0) (table [95OFF/CAP]-2) and Δε(T) results (table [95OFF/CAP]-3) which also agree (within uncertainty) with Offerlé's original determinations (table [95OFF/CAP]-2 and 3).

The original E(T,I), or the E(T,0) and Δε(T) results of SIT regressions, were fitted to second order polynomial approximations about 25°C. The first order E'(T°,I) or Δε'(T°) term, and the second order E"(T°,I) / 2 or Δε"(T°) / 2 term were related to the corresponding entropy and heat capacity changes by using classical thermodynamic equation (T° = 298.15 K). This approximation is valid when heat capacity does not vary with T (which is certainly not the case) or has little effect. To check this (last) assumption three different ways of using this type of approximation were used:

$$F\,E(T,I) \approx F\,E(T°,I) + (T - T°)\,\Delta_rS(T°,I) + (T - T°)^2\,\Delta_rCp(T°,I) / (2T°)$$

$$F\,E(T,I) \approx F\,E(T°,I) + (T - T°)\,\Delta_rS(T°,I) - (T - T° - T\ln(T / T°))\,\Delta_rCp(T°,I)$$

$$F\,E(T,I) / T \approx F\,E(T°,I) / T - (1/T - 1/T°)\,\Delta_rH(T°,I) + (1/T - 1/T°)^2\,T°^2\,\Delta_rCp(T°,I) / 2$$

The second one is obtained assuming constant Δ_rCp. The first and third ones are second order Taylor's series expansion, neglecting then the variation of the Δ_rCp with temperature. Consistent numbers were found whatever the equation used. The plot of the experimental data E (figure [95OFF/CAP]-1) or E/T (figure [95OFF/CAP]-2) as a function of T or respectively 1/T, showed nearly straight lines. This means that the variations with temperature of the corresponding entropy change, Δ_rS, or respectively of Δ_rH are small, hence Δ_rCp effect on E or E/T is small. Unfortunately this does not mean that Δ_rCp is constant; but only that it is difficult to detect its influence on E in the temperature range studied, only an overall mean value can then be estimated. Setting Cp to zero usually does not change E (or E/T) and Δ_rS (or Δ_rH) values within uncertainty. Adding the data at 60°C (to those between 5 and 55°C) has small effect, except for the data extrapolated to zero ionic strength. The scattering of the data at 60°C and the lack of points at the lowest ionic strength probably explains the fact the different shape of the extrapolating curve to zero ionic strength at 60°C, when comparing with similar SIT approximation at

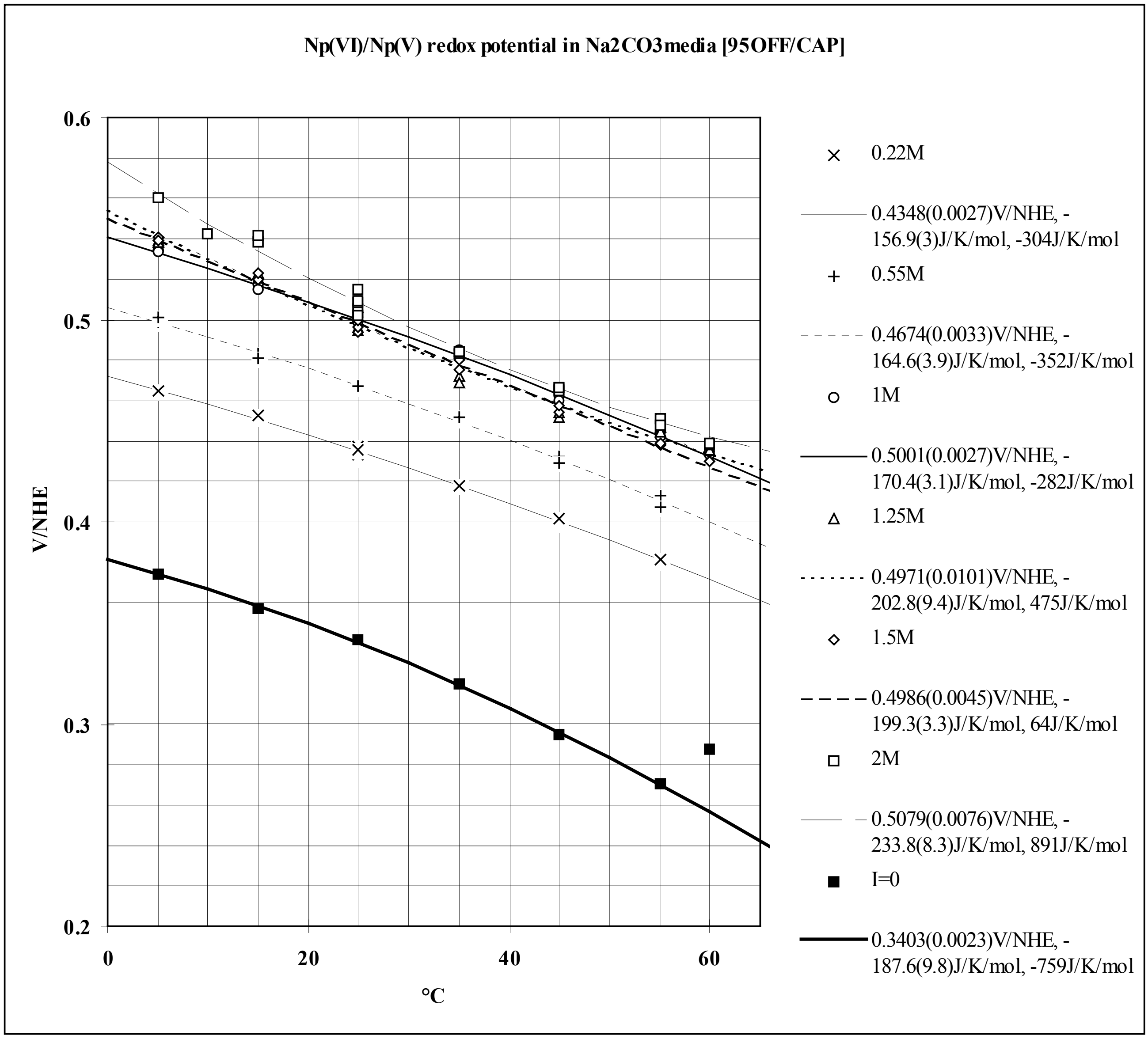


Figure [95OFF/CAP]-1: Temperature influence on the Np(VI)/Np(V) redox potential in Na_2CO_3 media. Experimental data, E(T,I), [95OFF/CAP] were fitted to a second order polynomial equation. From the zero, first and second order term, E(T°,I), $\Delta_rS(T°,I)$ and $\Delta_rCp(T°,I)$ values (written on the figure) were calculated. For I = 0, they are standard values. T° = 298.15 K.

the other temperatures (figure [95OFF/CAP]-1). For this reason, and because this review uses Δ_rG, Δ_rH and Δ_rS data at 25°C, their values were finally calculated by using the local (about 25°C) approximation with the directly measured data: i.e. second order polynomial regression of E as a function of (t - 25°C). This was also the procedure used by Offerlé who obtained practically the same numbers as those recalculated by this review (table [95OFF/CAP]-4) except for Δ_rCp specially at zero ionic strength; but it is still within uncertainty.

The variations of $\Delta\varepsilon$ with temperature were also fitted to a second order polynomial expression (figure [95OFF/CAP]-5): this review results agree with Offerlé's ones [95OFF/CAP] (table [95OFF/CAP]-3). As above, the second order term could not be determined with high accuracy, since it has small influence in the experimental conditions studied. The polynomial expression can then again be interpreted as a second order Taylor's series expansion: the fitted coefficients of the polynomial expression are then estimations of $\Delta\varepsilon$ derivatives with temperature, $\Delta\varepsilon'$ and $\Delta\varepsilon''/2$. As proposed [94GIF/VIT] by the same laboratory. $\Delta\varepsilon'$ and $\Delta\varepsilon''$ were then used with classical thermodynamic equations to extrapolate Δ_rS, Δ_rH and Δ_rCp to zero ionic strength (figures [95OFF/CAP]-4). As for E (or $\log_{10}K$) when using

$$E_{T,I}\,F/(R\,T\,\ln 10) \quad + \Delta z^2\,D_{T,I} \quad = E_{T,0}\,F/(R\,T\,\ln 10) \quad + m\,\Delta\varepsilon_T$$

the Δ_rS, Δ_rH and Δ_rCp data are corrected for the Debye-Hückel term, and the plot of the resulting points are straight lines (within uncertainties) whose slope are related to $\Delta\varepsilon'$ and $\Delta\varepsilon''$ according to the following equations that were used by this review for T = T° (= 298.15 K):

$$\Delta_rH_{T,I}/(R\,T\,\ln 10) \quad + \Delta z^2\,T\,D'_{T,I} \quad = \Delta_rH_{T,0}/(R\,T\,\ln 10) \quad + m\,T\,\Delta\varepsilon'_T$$

$$\Delta_rS_{T,I}/(R\,\ln 10) \quad + \Delta z^2\,(D_{T,I} + T\,D'_{T,I}) \quad = \Delta_rS_{T,0}/(R\,\ln 10) \quad + m\,(\Delta\varepsilon_T + T\,\Delta\varepsilon'_T)$$

$$\Delta_rCp_{T,I}/(R\,\ln 10) \quad + \Delta z^2\,(2\,T\,D'_{T,I} + T^2\,D''_{T,I}) \quad = \Delta_rCp_{T,0}/(R\,\ln 10) \quad + m\,(2\,T\,\Delta\varepsilon'_T + T^2\,\Delta\varepsilon''_T)$$

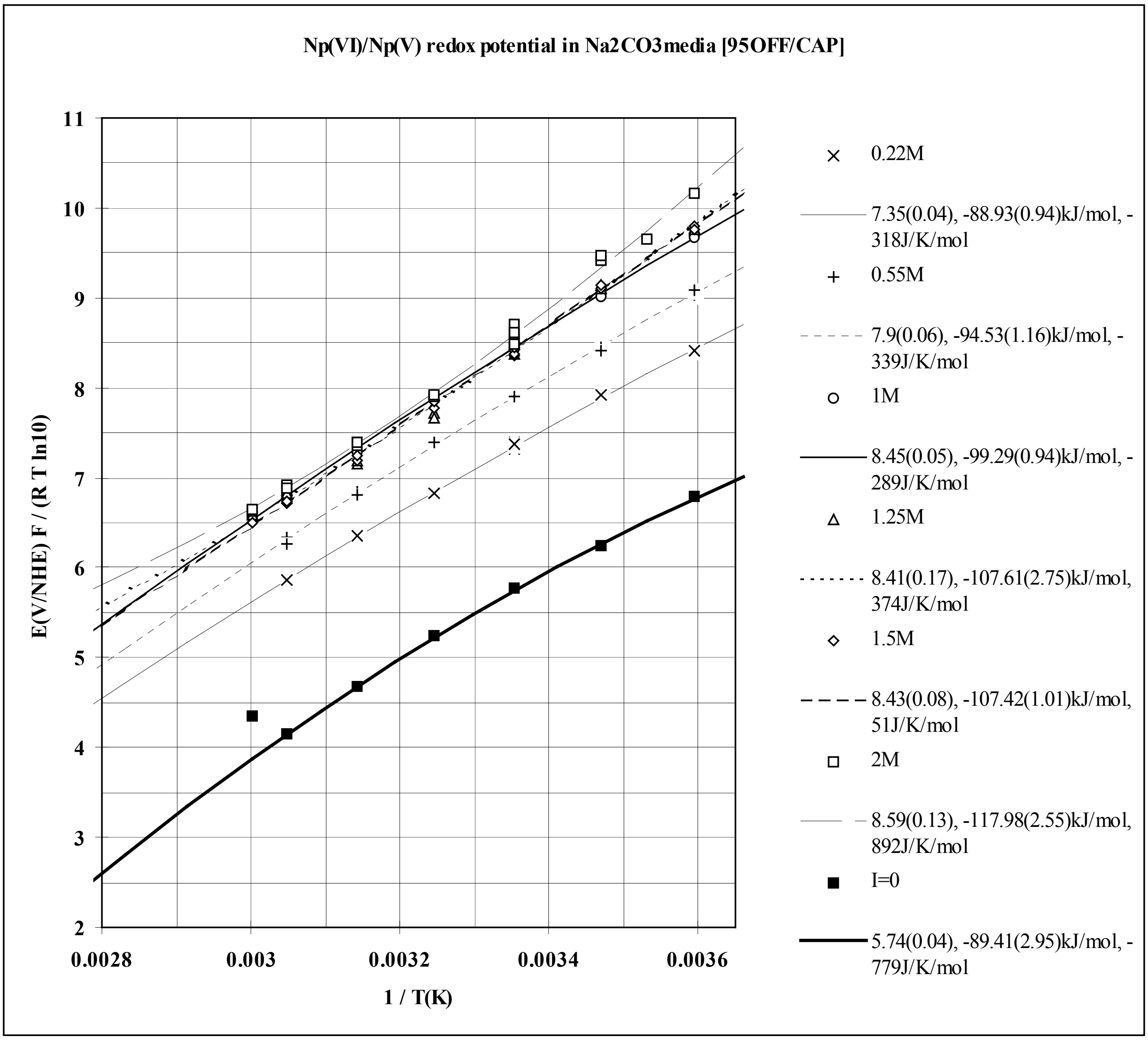


Figure [95OFF/CAP]-2: Temperature influence on the equilibrium constant of the Np(VI)/Np(V) redox couple in Na_2CO_3 media. From the experimental data, E(T,I), [95OFF/CAP] $\log_{10}K(I,T) = F\ E(T,I) / (R\ T\ \ln 10)$ were calculated, and then fitted to a second order polynomial equation as a function of 1/T. From the zero, first and second order term, $\log_{10}K(T°,I)$, $\Delta_rH(T°,I)$ and $\Delta_rCp(T°,I)$ values (written on the figure) were calculated. For I = 0, they are standard values. T° = 298.15 K.

Using these equations either to predict ionic strength influence on Δ_rS, Δ_rH and Δ_rCp, or to extrapolate the corresponding data to zero ionic strength gave consistent data (table [95OFF/CAP]-6 and figures [95OFF/CAP]-4).

All these calculations finally show that consistent results were found in the (relatively narrow) temperature domain studied and in a wide range of ionic strength conditions:

- Δ_rCp and $\Delta\varepsilon''_T$ (second order) term have nearly negligible influence,
- different data treatment using constant Δ_rCp approximation, in different ways gave consistent results,
- in some data treatments, extrapolation to zero ionic strength was first performed (to typically obtain $E_{T,0}$ from $E_{T,I}$ data), and then temperature polynomial regression produced the standard values ($E_{T°,0}$, $\Delta_rS_{T°,0}$, $\Delta_rH_{T°,0}$ and $\Delta_rCp_{T°,0}$). In other data treatments, temperature polynomial regression was performed first (to typically obtain $E_{T°,I}$, $\Delta_rS_{T°,I}$, $\Delta_rH_{T°,I}$ and $\Delta_rCp_{T°,I}$ from $E_{T,I}$ data) and then extrapolation to zero ionic strength produced the same standard values within uncertainty.
- The data proposed originally by Offerlé, agree well with those calculated by this review.
- Two (small) corrections were disregarded by the authors, and by this review because they are only known at 25°C: dissociation of the Np(V) limiting complex (see below) and [89RIG] difference between the diffusion coefficients of the two limiting complexes (that were the major electroactive species).

The normal potential measured at 25°C are consistent (figure [95OFF/CAP]-6) with the other data [89RIG, 77SIM] selected by this review. For this comparison, the original data were corrected for dissociation of the Np(V) limiting complex (table [95OFF/CAP]-7). This correction changes the final results E° and $\Delta\varepsilon$, by $-3._9$ mV and 0.02_1 $kg.mol^{-1}$ respectively. This is less than the uncertainty (table [95OFF/CAP]-7). This correction was disregarded for the data in K_2CO_3 media, for the data at other temperatures and for the data not selected by this review, because the parameters needed for this calculation are not known and it is not certain that any usual estimating of these small corrections would go in the right direction.

These [95OFF/CAP, 89RIG, 77SIM] data agree very well. Some other data ([93LI/KAT], one of those reported in [81WES/SUL]) also agree; they are not used by this review for lack of information on the calibration of the reference

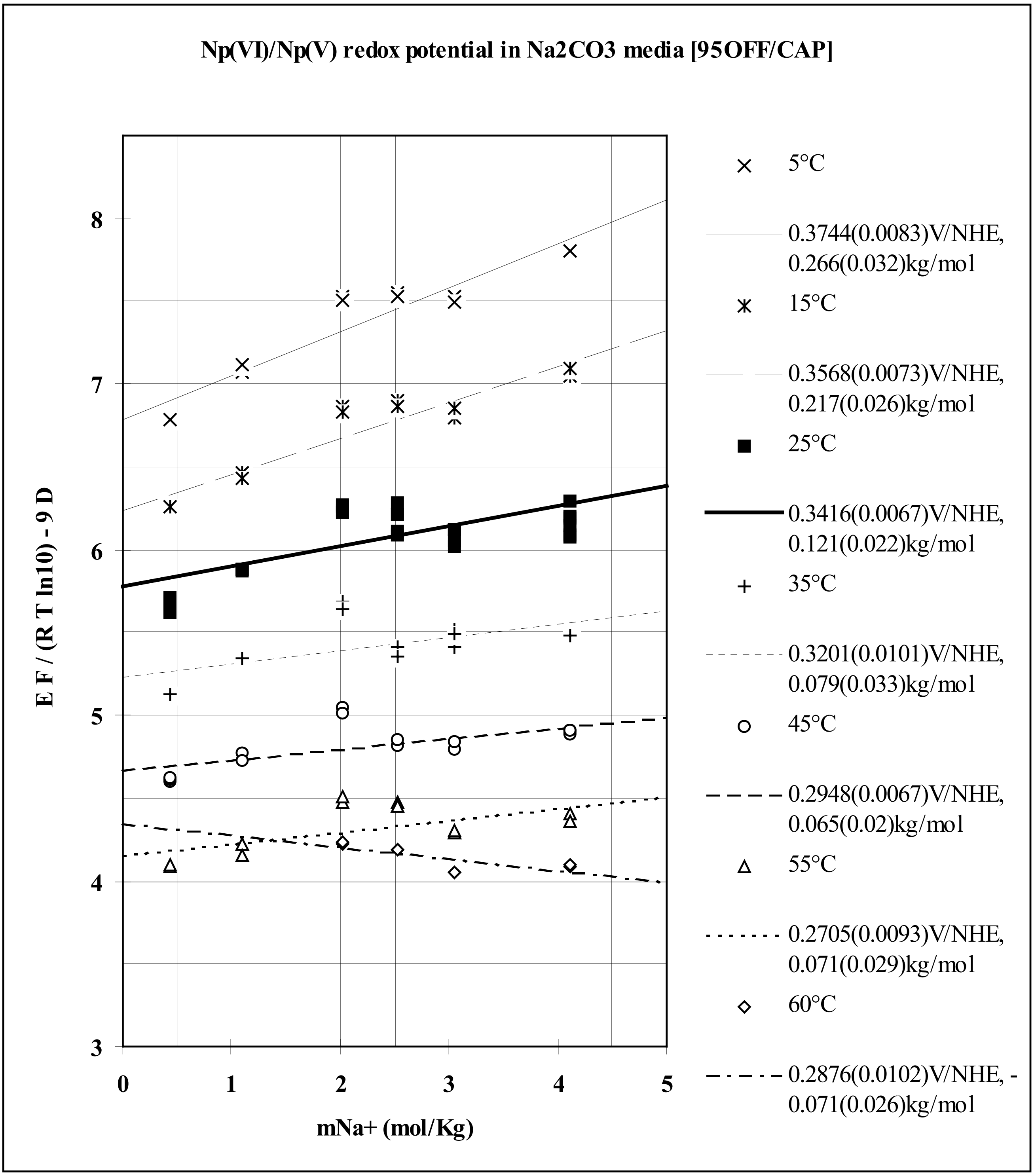


Figure [95OFF/CAP]-3: Extrapolation to zero ionic strength of the Np(VI)/Np(V) redox potential at different temperatures. The E(T,0) and Δε(T) written on the figure, are the results of SIT linear regressions performed at each temperature from the E(T,I) data measured by Offerlé [95OFF/CAP].

electrode. The other data [74SIM/VOL, 75SIM, 81WES/SUL, 84MAY, 84VAR/HOB] are systematically shifted toward lower potentials which can clearly be attributed to junction potential for some of them ([74SIM/VOL, 75SIM]), and since the shift increases with ionic strength, the same explanation possibly also stands for [84MAY] and [84VAR/HOB] works.

[95PAL/NGU]

Palmer D.A;, Nguyen-Trung C. Aqueous Uranyl Complexes. 3. Potentiometric Measurements of the Hydrolysis of Uranyl(VI) ion at 25°C J. Solution Chem. 24, 12 (1995) 1282-1291

[95VIT]

Vitorge P. *Neptunium en solution carbonate concentrée réductrice: bibliographie pour l'OCDE-AEN-TDB* (mostly in English) CEA-BIB-246 (1995)

This is a draft of the Np(IV) carbonate part of the present view, with more details, materials, figures and tables for internal discussion, with prepublication of experimental data on Np(IV) [95DEL/VIT] and Np(VI) [96OFF/CAP].

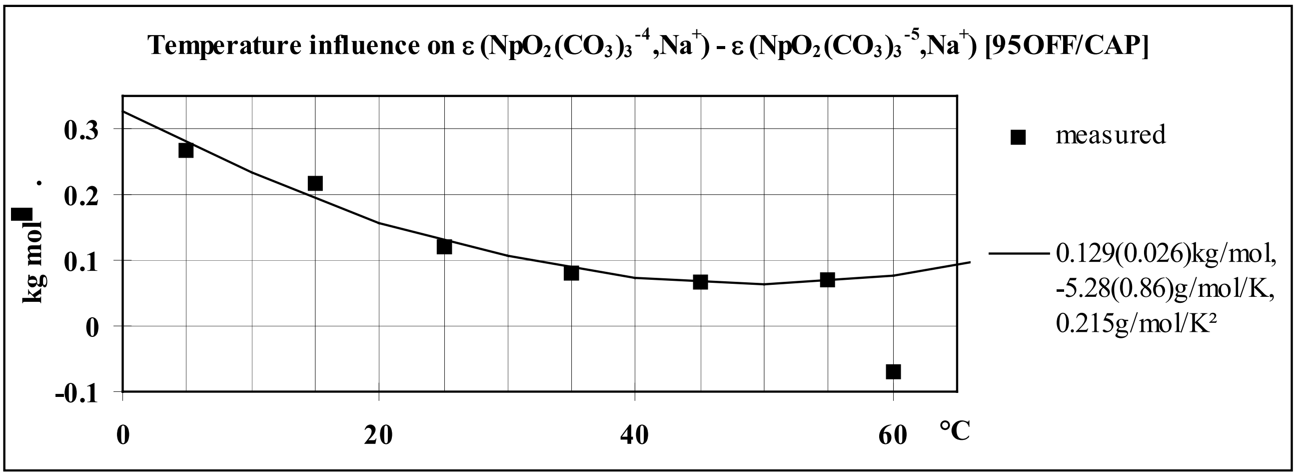


Figure [95OFF/CAP]-5: Temperature influence on the specific interaction coefficient change for the Np(VI)/Np(V) redox equilibrium in Na_2CO_3 media. The line is plotted with a second order polynomial equation. The fitted values of its zero, first and second order terms were used to obtain Δε(T°), Δε'(T°) and Δε"(T°) respectively written on the figure. The points are Δε(T) from the figure [95OFF/CAP]-3.

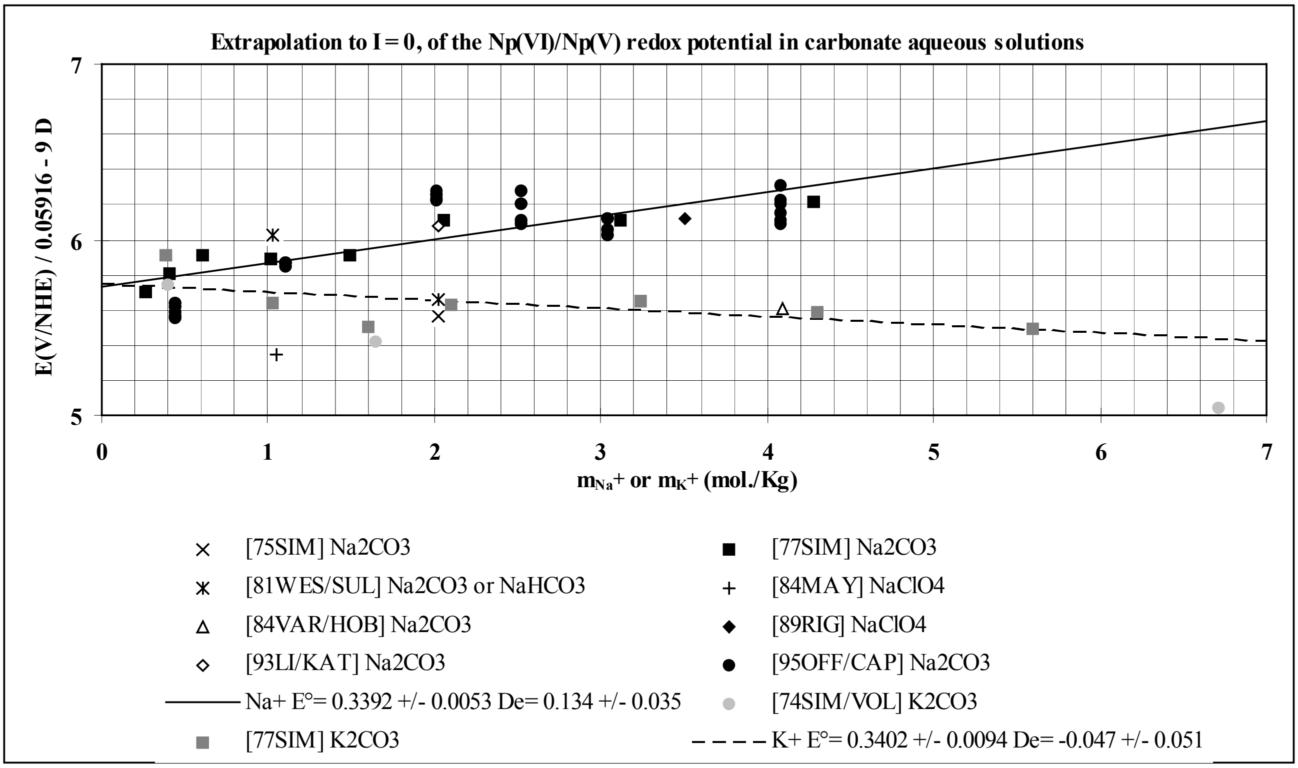


Figure [95OFF/CAP]-6: Extrapolation to zero ionic strength of the Np(VI)/Np(V) redox potential measured in Na^+ and K^+ carbonate media. The black and dark grey points were used for this extrapolation: These works from two different laboratories: Simakin [77SIM] and Vitorge [89RIG, 95OFF/CAP] ones, gave evidence of correct calibration of the reference electrode.

[96DEL/VIT]

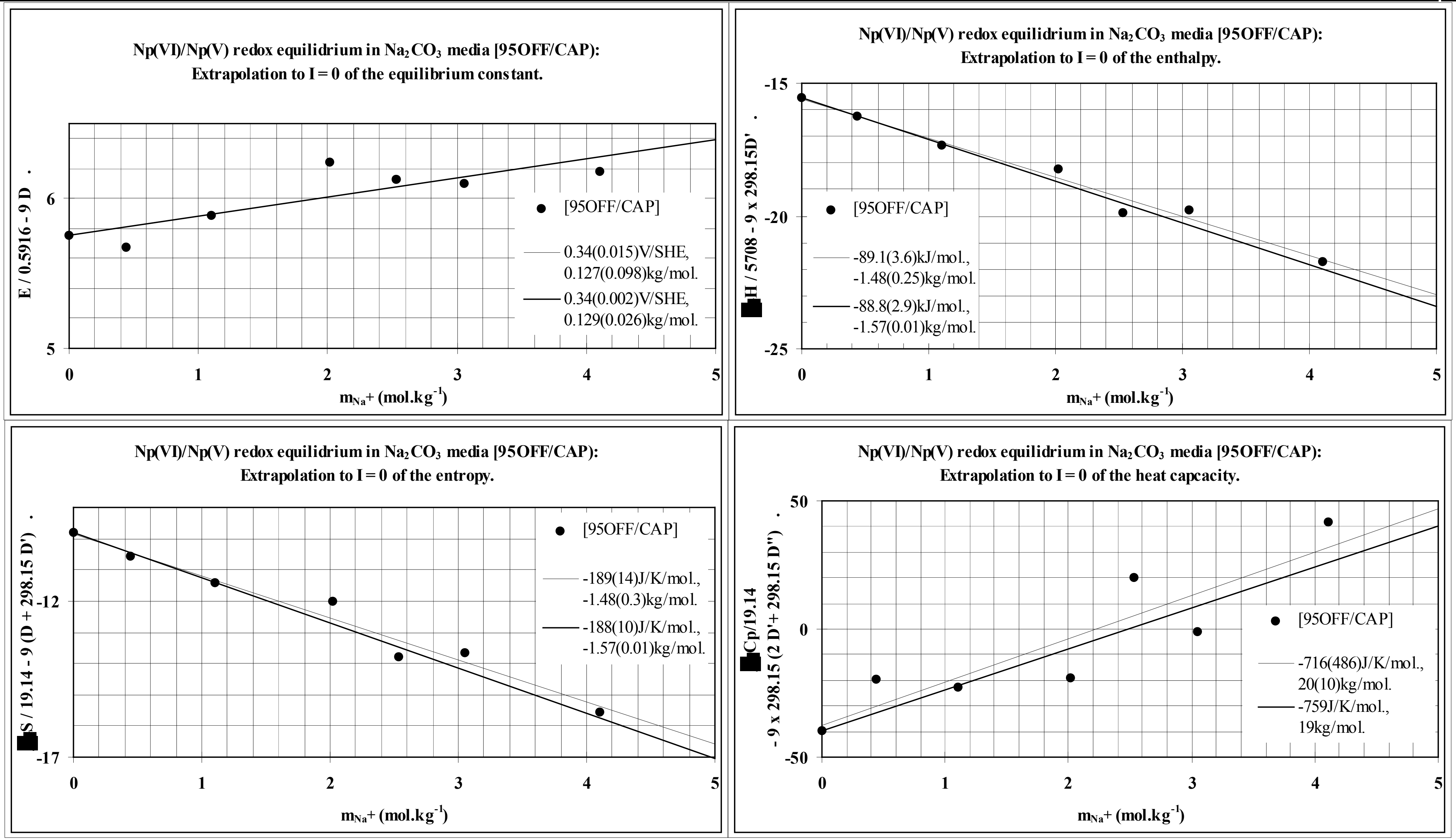
Delmau L.H., Vitorge P., Capdevila H. *Np(V)/Np(IV) en solutions carbonate/bicarbonate concentrées* CEA-N-2807 (1996) *(in French)*

[97VIT/CAP]

Vitorge P., Capdevila H. *Neptunium en solution aqueuse bicarbonate / carbonate oxydante.* (mostly in English) CEA-BIB to be published

This is a draft of the Np(VI) carbonate part of the present review, with more details, materials, figures, tables for internal discussion, and with supplementary experimental data on Np(VI) solubility. The authors estimated that equilibrium was not achieved in several samples. Still, using analogy with Uranium and Plutonium, they interpreted some of their data.

The only problem with this work is the equilibrium achievement that could not be controlled as pointed out by the authors. Since the authors took into account this problem in the interpretation of their data and uncertainty estimation, the formation constants produced by this [97VIT/CAP] work are accepted (table [97VIT/CAP]). When $[CO_3^{-2}] > 10\mu M$) a solid phase was probably slowly precipitating, possibly $Na_4NpO_2(CO_3)_{3(s)}$ whose solubility product was estimated. Most of the corresponding equilibrium constant values present small monotonous shift within the partial actinide series: Uranium, Neptunium and Plutonium.



Figures [95OFF/CAP]-4: Extrapolation to zero ionic strength of the normal potential, the enthalpy, entropy and heat capacity changes at 25°C from the redox potential measured by Offerlé [95OFF/CAP] at different temperatures in Na_2CO_3 media (not corrected for $NpO_2(CO_3)_3^{-5}$ dissociation). The points are the fitting results shown on the figure [95OFF/CAP]-1, except for enthalpy (figure [95OFF/CAP]-2). Thin lines are SIT linear regression, thick lines are predictions using the fitting results $\Delta\varepsilon$, $\Delta\varepsilon'$ and $\Delta\varepsilon''$ values (figure [95OFF/CAP]-5). Numerical values used to plot these lines are written on the figure: ($E°$, $\Delta\varepsilon$), ($\Delta_rH°$, $T°\ \Delta\varepsilon'$), ($\Delta_rS°$, $T°\ \Delta\varepsilon$) and ($\Delta_rC_p°$, $T°^2\ \Delta\varepsilon''$) values in parenthesis are uncertainties (1.96 σ on linear regressions).

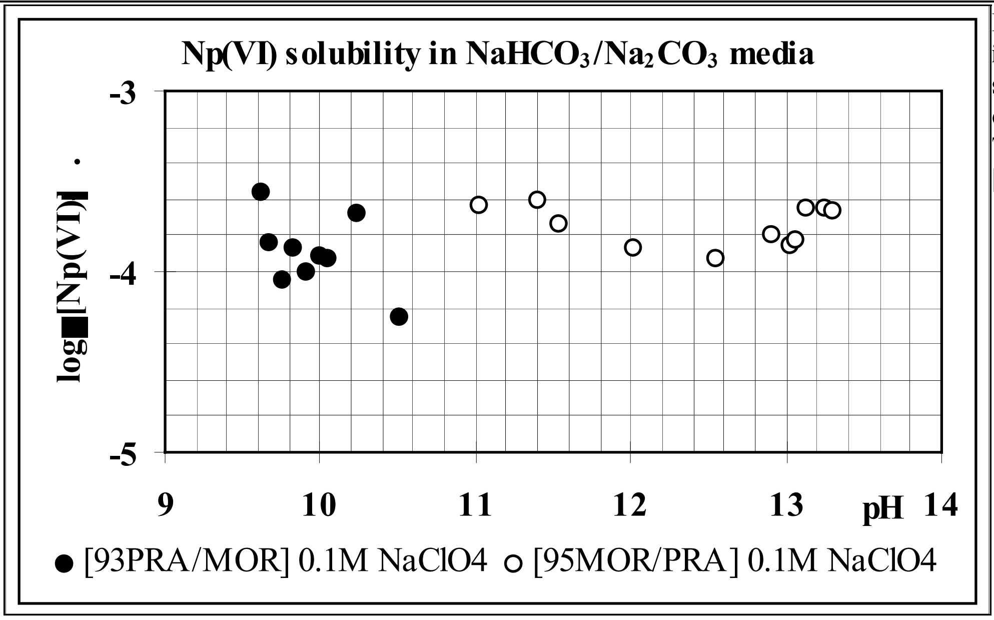


Figure [95MOR/PRA]: pH influence on Np(VI) solubility in bicarbonate / carbonate aqueous solutions. This figure is a detail of figure [97VIT/CAP]-1

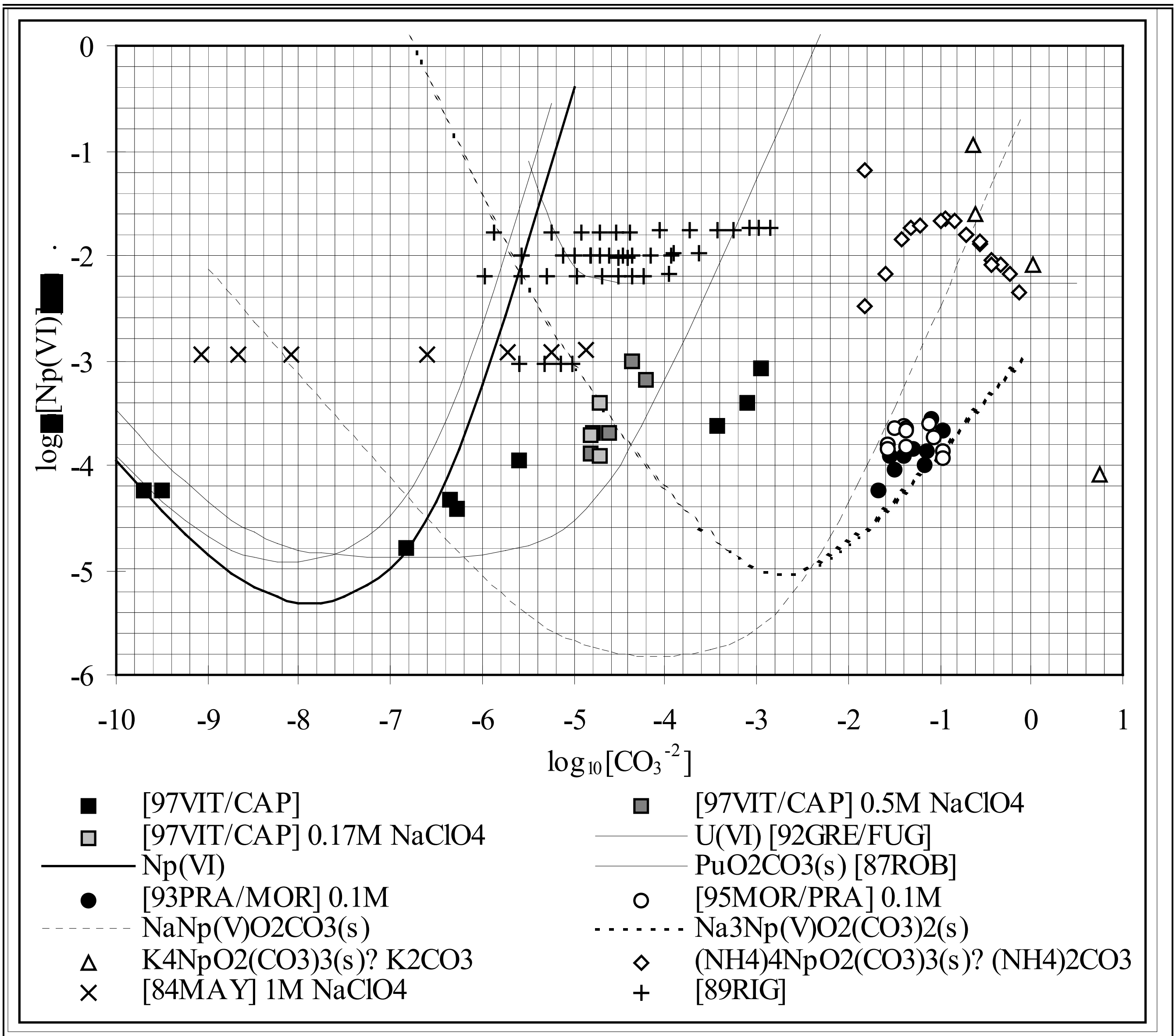
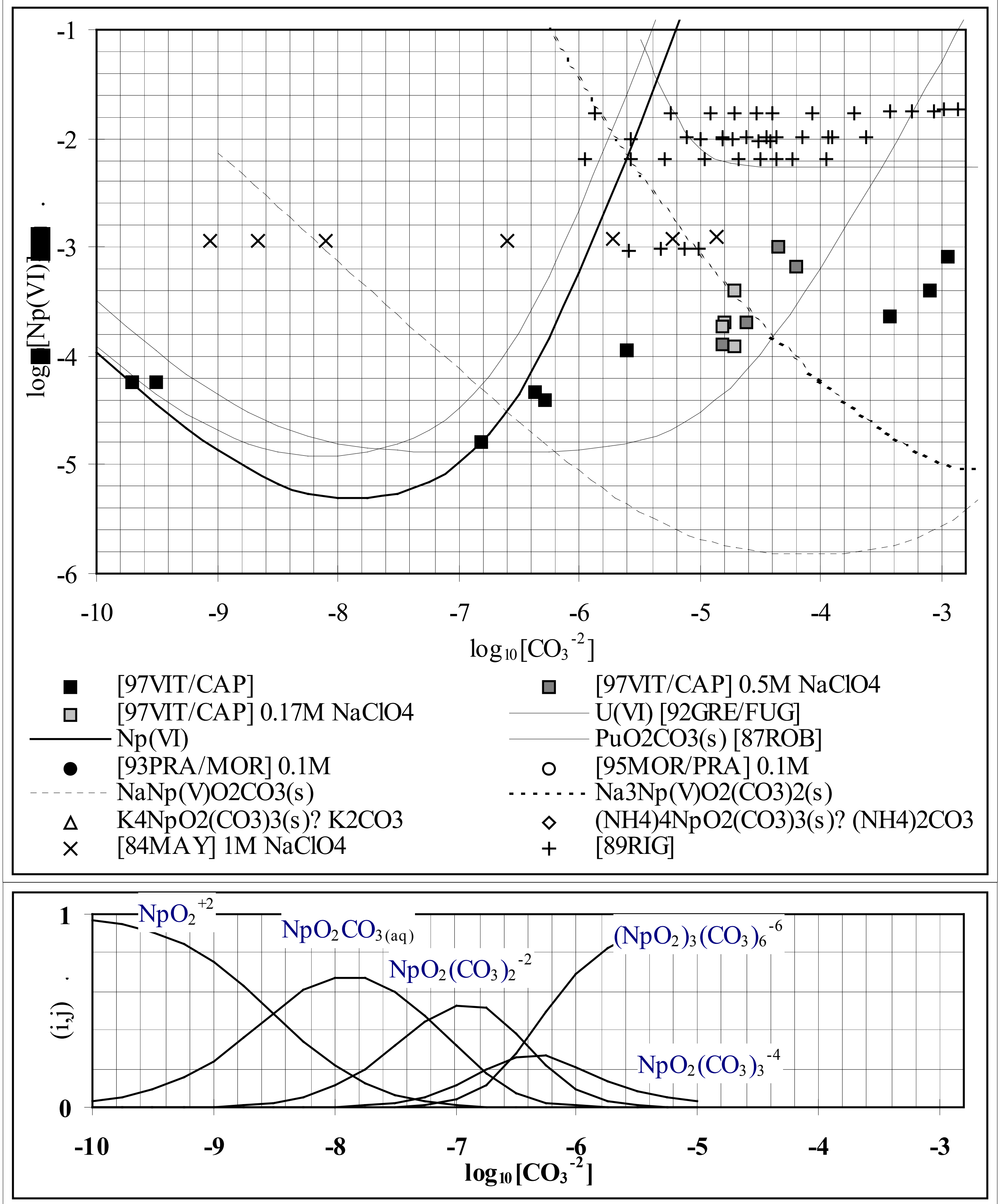
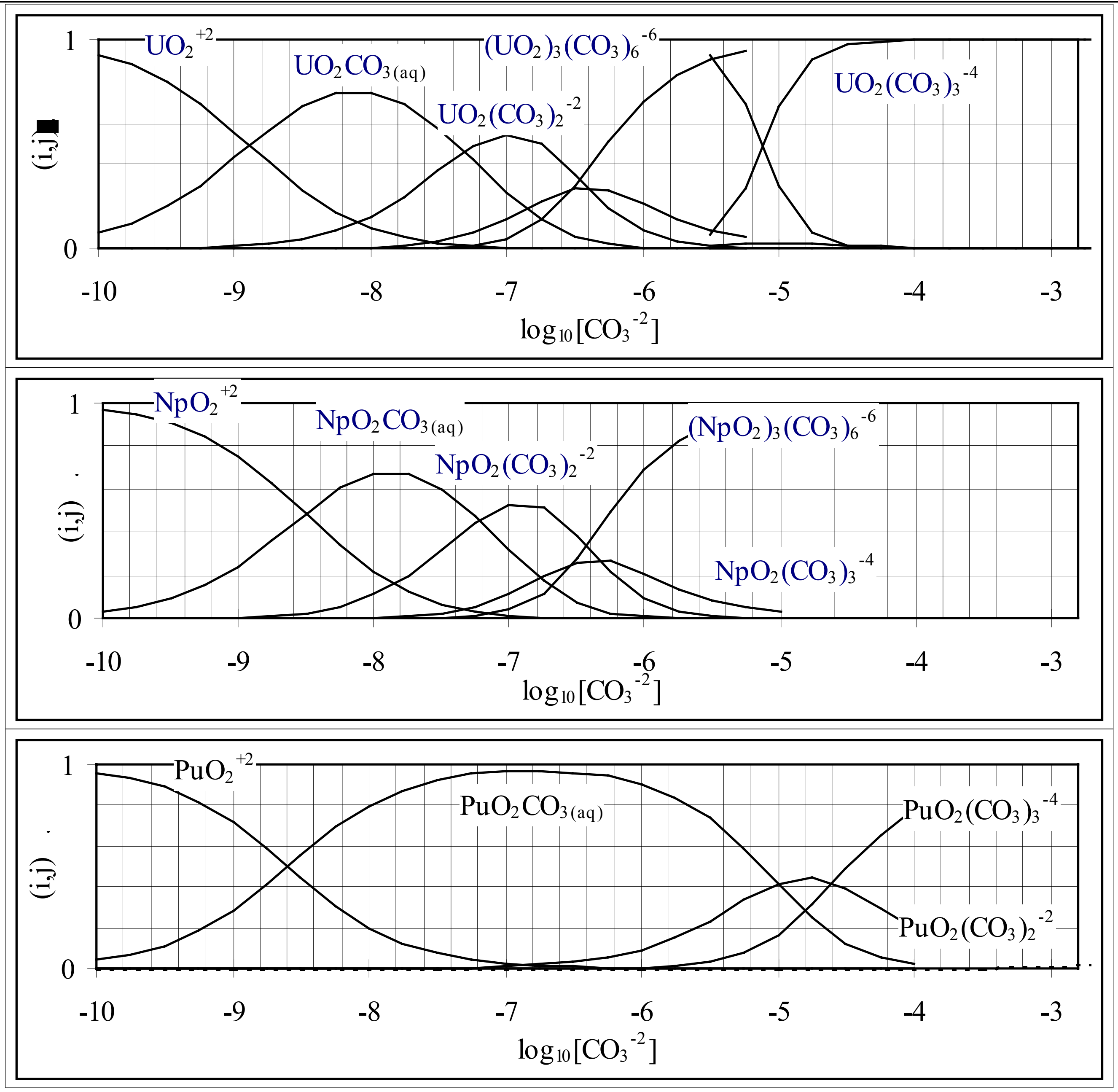


Figure [97VIT/CAP]-1: Np(VI) solubility in bicarbonate / carbonate aqueous solutions. Room temperature, 3 M $NaClO_4$ excepted when other conditions are stated. [93PRA/MOR] and [95MOR/PRA] experimental data are the same as in the figure [95MOR/PRA]. [97VIT/CAP] data were measured at P_{CO_2} 1 atm. $AnO_2CO_{3(s)}$ (An = U, Np or Pu) and $Na_4AnO_2(CO_3)_{3(s)}$ solubilities (An = U or Np) are calculated (lines) with the equilibrium constants of the table [97VIT/CAP]. Discontinuity of the calculated curves corresponds to the transformation of the solid phase (into the other one). Potentiometric [84MAY] and spectrophotometric data where certainly obtained in oversaturated solutions.



Figures [97VIT/CAP]-2: Np(VI) speciation in bicarbonate / carbonate aqueous solutions equilibrated with $NpO_2CO_{3(s)}$ solid phase. Room temperature, 3 M $NaClO_4$ excepted when other conditions are stated. The solubility figure, is a part of figure [97VIT/CAP]-1. Speciation is calculated with the same constants as the solubility curve. Actually precipitation is slow enough to observe the trinuclear species practically pure [86GRE/RIG, 89RIG] during at least 30 minutes and slow precipitation was effectively observed during this observation [86GRE/RIG, 89RIG]. This could be due to $Na_4NpO_2(CO_3)_{3(s)}$ or other (unknown) possible solid phase of CO_3/NpO_2 stoichiometric ratio among 1 to 3. Note [86GRE/RIG, 89RIG] spectrophotometric measurements were performed up to Np(VI) precipitation, which is consistent with $NpO_2CO_{3(s)}$ solubility as extrapolated by this review from [97VIT/CAP] data.

Pratopo's data [93PRA/MOR, 95MOR/PRA] were probably out of equilibrium. In the same way, no equilibrium constant for soluble species is proposed by this review, in opposition to what did his thesis. All the published Np(VI) solubility measurements in these conditions ($[CO_3^{-2}] > 10\mu M$) are quite scattered (figure [97VIT/CAP]-1), some of them plotted in log-log representation are possibly parallel to $UO_2CO_{3(s)}$ solubility curves in small domains; but extracting numbers from this type of observation, lead to contradiction with other published solubility works. The slow transformation from one solid phase ($NpO_2CO_{3(s)}$) to another one ($Na_4NpO_2(CO_3)_{3(s)}$ or $NpO_2(OH)_{2(s)}$) can as well explain this type of



Figures [97VIT/CAP]-3: Np(VI) speciation in bicarbonate / carbonate aqueous solutions equilibrated with $AnO_2CO_{3(s)}$ or $Na_4UO_2(CO_3)_{3(s)}$ solid phase. Room temperature, 3 M $NaClO_4$. The Np(VI) figure, is the same as the speciation part of figure [97VIT/CAP]-2. U(VI) speciation is calculated with the same constants as the solubility curve assuming equilibrium with the most stable of the two solid phases. Discontinuity of the calculated curve corresponds to the transformation of the solid phase (into the other one). Quite regular shift of the equilibrium constant and the corresponding stability domains, are observed along the partial actinide series U, Np and Pu; but the experimental determination of $PuO_2CO_{3(aq)}$ stability [87ROB/VIT] used to plot this figure, was probably overestimated. The trinuclear Plutonium species is the most difficult species to detect among the U, Np and Pu series; but it was nevertheless observed in oversaturated solutions as for Np(VI).

missy straight lines for single series of measurements, since the equilibrium of soluble species is usually faster than transformation within the bulk of the solid phase.

The equilibrium constants extracted from Np(VI) solubility works are consistent with the corresponding U and Pu ones as already observed above. In the same way, regular trends are observed for speciation predicted by using these values (figure [97VIT/CAP]-3). These calculations confirm [86GRE/FUG] the trinuclear carbonate species is more stable for Uranium (it varies as U > Np > Pu), and it was hence observed only in oversaturated solutions for Plutonium.

Supplementary materials

Nous profitons de la publication de la présente note bibliographique, pour rendre accessible des données supplémentaires issues de notre laboratoire.

Table [97VIT/CAP]-1: Carbonate Np(VI) equilibrium constants estimated from solubility measurements and comparison with the U(VI) and Pu(VI) ones, at room temperature, in 3 M $NaClO_4$ aqueous solutions. The values fitted from [97VIT/CAP] solubility measurements are bolded. They are compared to the corresponding Uranium [84GRE/FER, 92GRE/FUG, 95SIL/BID] and Plutonium [87ROB] and other values selected by this review. For β1 and β_2, I corrections are estimated to be equal to the U ones (when no other values are available). $\beta_i = [MO_2(CO_3)_i^{2-2i}] / [MO_2^{2+}] [CO_3^{-2}]^i$), $\beta_{6,3} = [(MO_2)_3(CO_3)_6^{-6}] / [MO_2^{2+}]^3 [CO_3^{-2}]^6$), $Ks = [MO_2^{2+}] [CO_3^{-2}]$. Regular progression within the partial actinide series (M = U, Np, Pu) is observed for most of the formation constant and solubility product values. Δ_rG (kJ.mol.¯1) values are tabulated in the last line.

$lg\beta_1$		$lg\beta_2$		$lg\beta_3$		$lg\beta_{6,3}$-3$lg\beta_3$		lgK_s		$lg\beta_{6,3}$			I
9.07	± 0.22	16.19	± 0.24	22.61	± 0.18	-11.43	± 1.39	-13.95	± 0.15	56.40	± 1.28	U	3
8.5	**± 0.97**	**15.72**	**± 0.51**	22.05	± 0.88	-10.06	± 0.56	**-13.98**	**± 0.38**	56.10	± 2.69	Np	3
8.6		13.6		18.2		-8.8		-13.5		45.8		Pu	3
8.47	± 0.06	15.72	± 0.12	21.75	± 0.06	-10.89	± 1.02	-13.30	± 0.05	54.36	± 1.01	U	0.5
7.90	± 0.99	15.25	± 0.56	19.75	± 0.29	-8.54	± 1.20	-13.33	± 0.42	50.72	± 1.49	Np	0.5
9.67	± 0.05	16.94	± 0.12	21.60	± 0.05	-10.80	± 1.01	-14.49	± 0.04	54.0	± 1.0	U	0
9.10	± 0.99	16.47	± 0.58	19.35	± 0.27	-8.27	± 2.35	-14.52	± 0.43	49.78	± 2.48	Np	0
-51.96	± 5.66	-93.99	± 3.30	-110.46	± 1.52	47.22	±13.42	82.86	± 2.46	-284.15	±14.18	Np	0

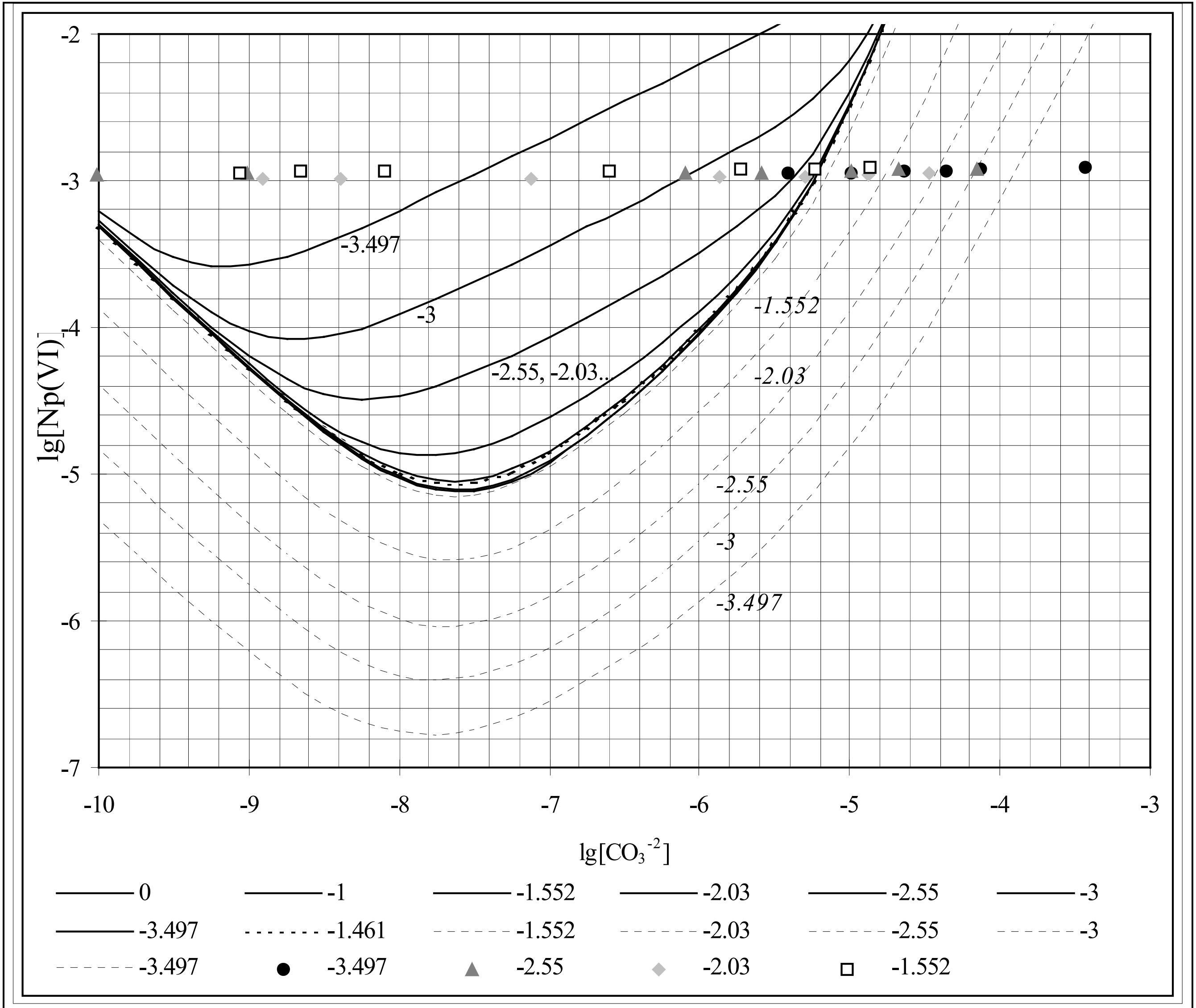


Figure [97VIT/CAP]-4: CO_2 partial pressure influence on Np(VI) solubility. Room temperature, 1 M NaClO4. Numbers are lgP_{CO_2}(atm) (lg is log_{10}). Points are experimental conditions of Maya's potentiometric titration [84MAY]. Solid and dashed lines are $NpO_2CO_{3(s)}$ ($lgK_{s0,1}$ = -13.314) and $NpO_2(OH)_{2(s)}$ (lg^*K_{s0} = 5.359) calculated solubilities respectively, using $lg\beta_{1,0,1} = 7.879$, $lg\beta_{1,0,2} = 15.201$, $lg\beta_{1,0,3} = 20.167$, $lg\beta_{3,0,6} = 51.691$, $lg\beta_{2,3,1} =-3.95$, $lg\beta_{3,5,0} = -22.07$, $lg\beta_{1,1} = -6.44$, $lg\beta_{2,2} = -9.23$, where $\beta_{i,j,k} = [(NpO_2)_i(OH)_j(CO_3)_k] [H^+]^j / [CO_3^{-2}]^k$, $\beta_{i,j} = \beta_{i,j,0}$. Thermodynamic solubility is the lowest one: $NpO_2CO_{3(s)}$ is transformed into $NpO_2(OH)_{2(s)}$ at $lgP_{CO_2} = -1.461 \pm 2.046$ (this high uncertainty is mainly du to lg^*K_{s0}). See also figures [97VIT/CAP]-2.

Table [97VIT/CAP]-2: $NpO_2(CO_3)_2^{-2}$ formation constant estimated from solubility measurements: sensitivity analysis. $\log_{10}K_s$ and $\log_{10}\beta_1$ values are fitted to [97VIT/CAP] solubility measurements fixing $\log_{10}\beta_3 = 22.054$, $\log_{10}\beta_{3,6} = 56.062$ and the tabulated $\log_{10}\beta_2$ values. Speciation (figures [97VIT/CAP]-2) shows that $\log_{10}K_s$ is readily obtained while there are not really enough data to fit $\log_{10}\beta_1$ and $\log_{10}\beta_2$ values. In addition there is a single reliable experimental measurement in chemical conditions where Np(VI) complexes are formed; bur reasonable $\log_{10}\beta_2$ values have little influence on calculated solubility (figures [97VIT/CAP]-2) due to formation of the limiting and trinuclear complexes in these conditions. Nevertheless, bolded values are proposed.

Σ	$\log_{10}K_s$	$\log_{10}\beta_1$	$\log_{10}\beta_2$	Σ	$\log_{10}K_s$	$\log_{10}\beta_1$	$\log_{10}\beta_2$	Σ	$\log_{10}K_s$	$\log_{10}\beta_1$	$\log_{10}\beta_2$
0.129	-14.062	9.167	12	0.161	-14.038	9.050	15.2	0.215	-13.998	8.770	15.6
0.129	-14.062	9.167	13	0.169	-14.031	9.014	15.3	0.240	-13.980	8.553	15.7
0.130	-14.060	9.161	14	0.181	-14.023	8.962	15.4	0.181	**-13.98**	**8.5**	**15.72**
0.135	-14.057	9.147	14.5	0.196	-14.012	8.888	15.5	0.274	-13.955	7.793	15.8
0.148	-14.047	9.097	15								

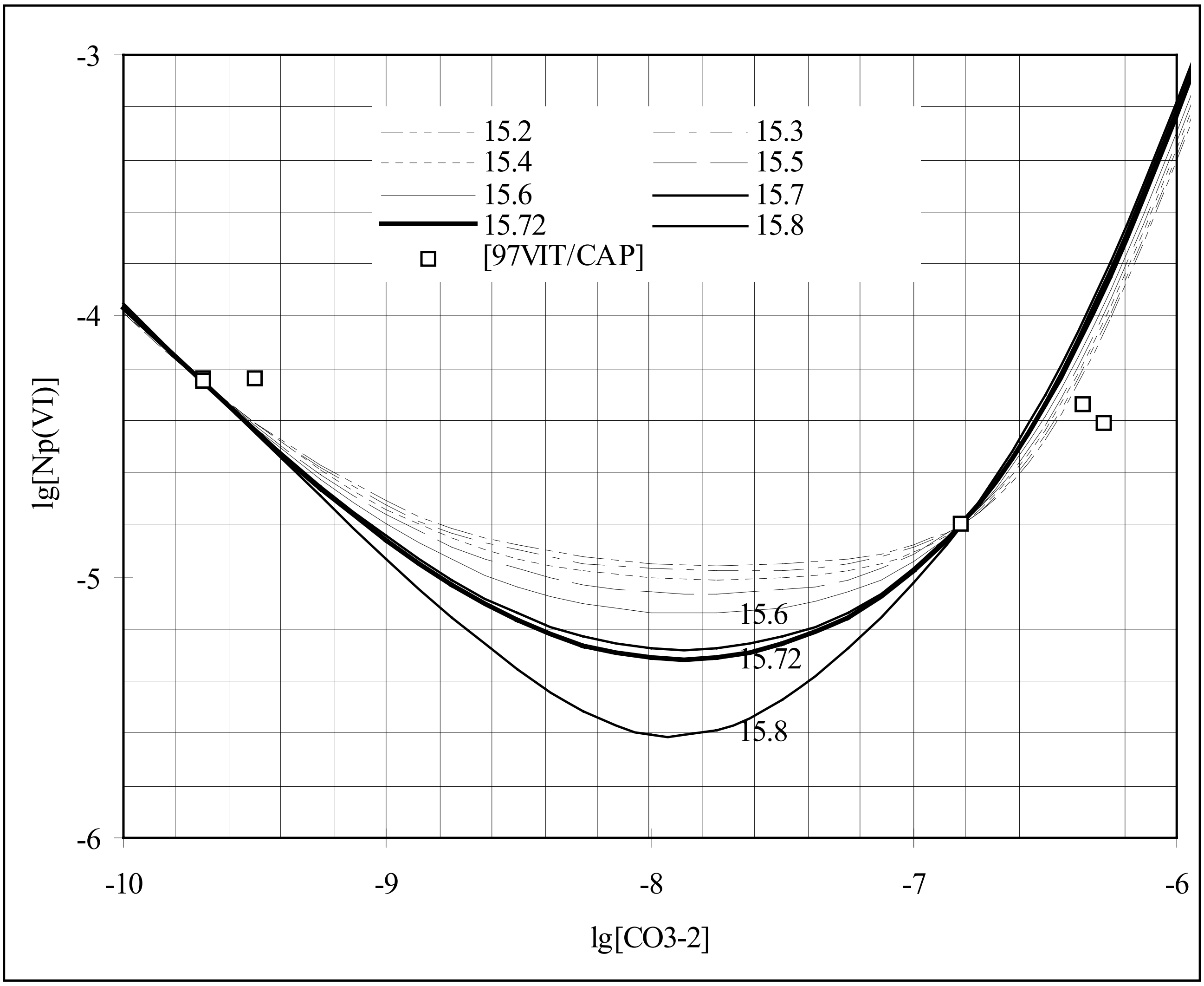


Figure [97VIT/CAP]-5: $NpO_2(CO_3)_2^{-2}$ formation constant estimated from solubility measurements: sensitivity analysis. Points are measured Np(VI) solubility [97VIT/CAP] as already reported in figures [97VIT/CAP]-1 and 2. Curves are plotted by using table [97VIT/CAP]-2 formation constants.

[95OFF/CAP]

Sophie Offerlé a vérifié la stabilité de son électrode de référence. Elle a en effet contrôlé avant et après chaque cycle de température (pour une force ionique donnée) si l'électrode de référence avait subi une éventuelle détérioration. Pour ce faire, elle a mesuré la différence de potentiel entre son électrode Ag/AgCl et une identique réservées à cet effet. Elle a ainsi constaté des écarts n'excédant pas 1,2 mV et une dérive inférieure à 0,2 mV. Ces valeurs ont été relevées dans son cahier de laboratoire et reportées dans les tableaux de résultats. Une électrode référence était un fil Ag/AgCl plongé dans un compartiment séparé rempli d'un mélange ($NaClO_4$, NaCl) de même force ionique que la solution de travail (afin de minimiser le potentiel de jonction qui a tout de même était mesuré à plusieurs reprises). Les résultats de mesure du potentiel de jonction n'ont pas été reportés dans le cahier de laboratoire; mais Sophie Offerlé précise qu'elle n'a jamais obtenu de valeur supérieure à 2 mV. on peut penser qu'il était maximum pour l'expérience en milieu Na_2CO_3 2 M où l'écart entre les concentrations de Na^+ de part et d'autre de la jonction est maximum.

[97VIT/CAP]

Ces mesures ont été commencées par Frédérique Coudray lors de son stage de DEA.

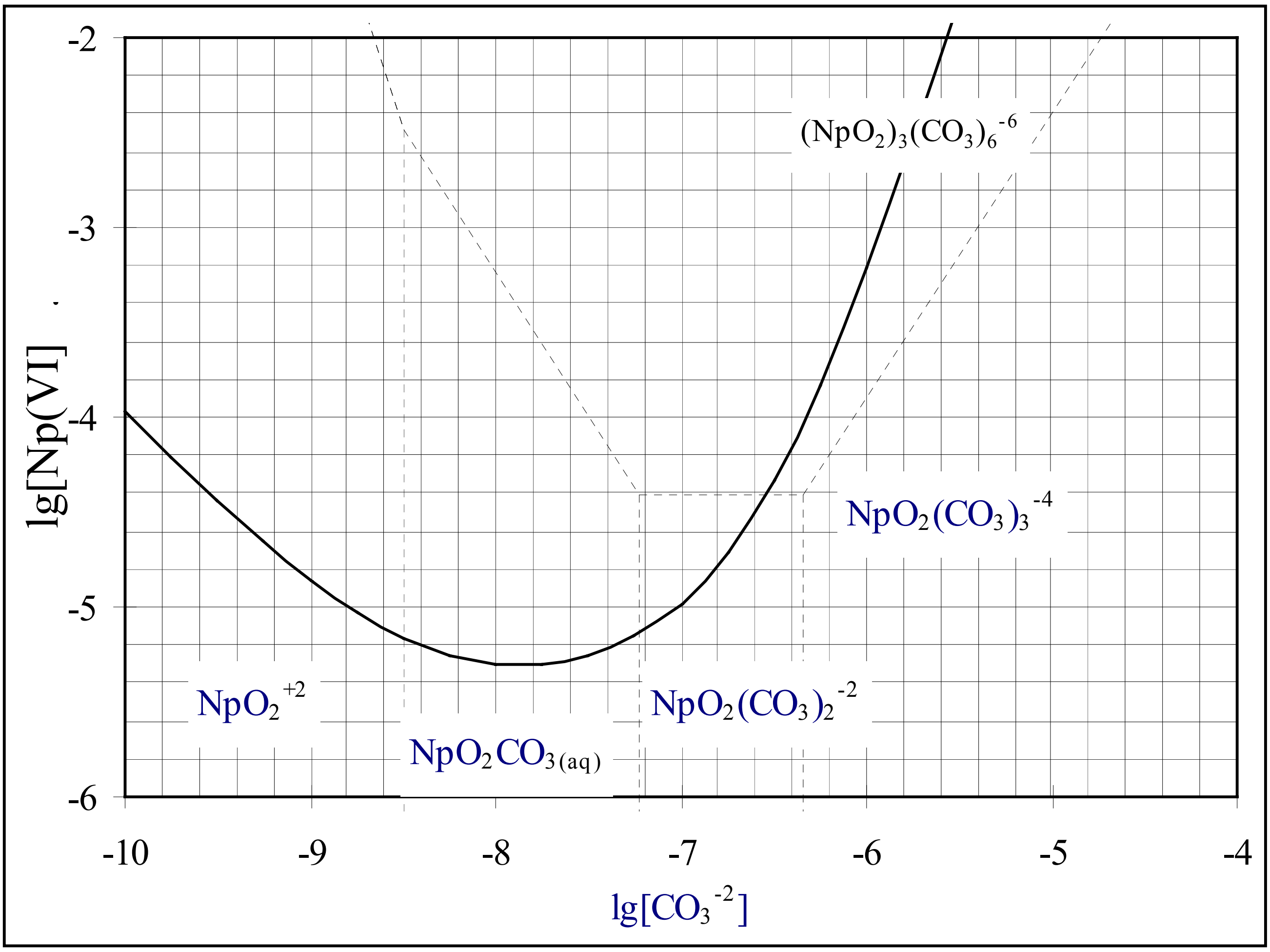


Figure [97VIT/CAP]-4: Np(VI) predominance diagram (dashed lines) and $NpO_2CO_{3(s)}$ solubility (solid line) at I=3M ($NaClO_4$) 25°C and P_{CO_2} high enough (typically more than 0.1 atm) to avoid hydrolysis. Equilibrium constants of table [97VIT/CAP]-1 were used to plot this diagram. As usual polynuclear species is stable in oversaturated solutions or in chemical conditions closed to precipitation. Other Na-Np(VI)-CO_3 solid phases precipitatein chemical conditions where $NpO_2(CO_3)_3^{-4}$ or $(NpO_2)_3(CO_3)_6^{-6}$ are formed (but no thermodynamic data could be estimated for them.

125 ml of Np(VI) mother solutions in 0.1 M $HClO_4$ were prepared and spectrophotometrically titrated as describe elsewhere [86GRE/RIG]. Np(VI) concentration was 0.106 m with less than 0.1 % of Np(V). The solid phase was obtained by precipitating the mother solution under $CO_{2(gas)}$ bubbling, adding small amounts of $NaHCO_{3(solid)}$, and waiting for pH stabilisation between each addition. From chemical analogy with U [92GRE/FUG] and Pu [87ROB] minimum Np(VI) solubility was expected at pH = 5, and from our previous studies [86GRE/RIG, 89RIG] it was known that Np(VI) precipitation was slow (slower than for U and Pu in similar conditions). $NaHCO_3$ addition was stopped at pH = 5, and precipitation occurred within a few days. For solubility measurements, Np(VI) was titrated by using liquid scintillation technique with a 1219 Rackbeta LKB spectrometer. α - β signals were electronically split. 1 ml of 1.04 to 10.4 µM Np(VI) solutions (from diluting mother solution) were added to 4 ml of the LKB Optiphase Hisafe 3 cocktail and used for calibration. Solubility measurements were performed similarly.

In a series of experiments, the Np(VI) solid was added to 0.01 M $HClO_4$ + 2.99 $NaClO_4$ solution. pH was varied by adding $HClO_4$ or $NaHCO_3$ solutions prepared at the same I ($NaClO_4$). Two other series were prepared at other ionic strengths (table [97VIT/CAP]-sup). Solubility was therefore obtained by dissolving $NpO_2CO_{3(s)}$ solid phase that was not characterised; but the same procedure had previously been used in our laboratory [86GRE/ROB] to study its X-ray diffraction pattern.

Unfortunately analysis of the results showed equilibrium was not achieved in several samples. Still, using analogy with U and Pu, tentative interpretation of the results is proposed in the following way. The $\log_{10}$solubility vs. $\log_{10}[CO_3^{-2}]$ plot (figure [97VIT/CAP]-1) fall about U [84GRE/FER, 92GRE/FUG] and Pu [87ROB] calculated solubilities. In our most acidic conditions ($\log_{10}[CO_3^{-2}]$ = -9.5 or -9.7) NpO_2^{+2} was certainly not complexed, K_s was then estimated from these data. Using this value, the β_3 and $\beta_{3,6}$ formation constants for ($NpO_2(CO_3)_3^{-4}$ and $(NpO_2)_3(CO_3)_6^{-6}$)) determined in this review, correct estimation of the solubility measurements at $\log_{10}[CO_3^{-2}]$ = -5.6 was obtained (without fitting extra parameter). K_s, β_1 and β_2 were then fitted (keeping the fixed β_3 and $\beta_{3,6}$ values). $NpO_2(CO_3)_2^{-2}$ formation constant (β_2) was the main parameter to get the correct fitting for $-9.7 < \log_{10}[CO_3^{-2}] < -6$; but it could not be easily fitted.

Table [95OFF/CAP]-sup: Enthalpy, entropy and heat capacity changes at 25°C for the Np(VI)/Np(V) redox equilibrium obtained from potential data measured in Na_2CO_3 aqueous solutions. The first column gives indications on the way the regressions were performed (see the foot notes). The second column is [Na_2CO_3]. 0 M [Na_2CO_3] data are calculated from the SIT regression results at each temperature (Table (95OFF/CAP]-2). Potential values are versus the NHE. F is the Faraday number. When mV is used (instead of volt), F value is taken in the corresponding units. The aim of this table is to check that the different ways to treat the data as a function of the temperature, are consistent: they lead to the same results within uncertainty. The selected (bolded) values correspond to the most direct determination, excluding the data at 60°C. The values calculated by Offerlé are in the lines [95OFF/CAP].

	(M)	n	E (V)	±	Δ_rH/F (V)	±	Δ_rS/F (mV.K^{-1})	±	$\Delta_rCp/(FT°)$ (mV.K^{-2})
[95OFF/CAP]	0		0.336	0.0094			-1.97	0.27	-0.006 ± 0.012
5 to 55°C, E(T)(a)	*0*	*6*	*0.3400*	*0.0017*	*-0.922*		*-1.951*		*-0.0122*
5 to 55°C E(T)(b)	**0**	**6**	**0.3403**	**0.0023**	**-0.920**	**0.026**	**-1.945**	**0.087**	**-0.0132±0.0049**
5 to 55°C, E(T), Cp°(c)	0	6	0.3403	0.0023	-0.922	0.026	-1.951	0.086	-0.0134±0.0050
5 to 55°C K(1/T)(d)	0	6	0.3398	0.0026	-0.927	.024	-1.969	0.081	-0.0135±0.0053
5 to 55°C, E(T)(a,e)	*0*	*6*	*0.3368*	*0.0032*	*-0.955*	*0.028*	*-2.073*	*0.092*	*0*
5 to 55°C E(T)(c,e)	0	6	0.3367	0.0035	-0.956	0.030	-2.076	0.101	0
5 to 55°C K(1/T)(d,e)	0	6	0.3367	0.0018	-0.950	0.031	-2.058	0.103	0
5 to 55°C, E(T)(a)	*0*	*7*	*0.3360*	*0.0247*	*-0.915*		*-1.941*		*0.0065*
5 to 60°C E(T)(b)	0	7	0.3356	0.0152	-0.914	0.161	-1.939	0.539	0.0057±0.0242
5 to 60°C, E(T), Cp°(c)	0	7	0.3361	0.0252	-0.911	0.159	-1.928	0.532	0.0059±0.0248
5 to 60°C K(1/T)(d)	0	7	0.3399	0.0021	-0.930	0.134	-1.979	0.449	-0.0147±0.0241
5 to 60°C, E(T)(a,e)	*0*	*7*	*0.3379*	*0.0037*	*-0.885*	*0.052*	*-1.835*	*0.175*	*0*
5 to 60°C E(T)(c,e)	0	7	0.3379	0.0038	-0.886	0.053	-1.837	0.178	0
5 to 60°C K(1/T)(d,e)	0	7	0.3374	0.0033	-0.890	0.049	-1.854	0.165	0
[95OFF/CAP]	0.22						-1.64		-0.0053
5 to 55°C, E(T)(a)	*0.22*	*6*	*0.4350*	*0.0016*	*-0.920*		*-1.625*		*-0.0057*
5 to 55°C E(T)(b)	**0.22**	**16**	**0.4348**	**0.0027**	**-0.920**	**0.017**	**-1.626**	**0.056**	**-0.0053±0.0030**
5 to 55°C, E(T), Cp°(c)	0.22	16	0.4348	0.0027	-0.920	0.017	-1.629	0.056	-0.0053±0.0030
5 to 55°C K(1/T)(d)	0.22	16	0.4348	0.0026	-0.922	0.015	-1.633	0.053	-0.0055±0.0031
5 to 55°C, E(T)(a,e)	*0.22*	*6*	*0.4335*	*0.0016*	*-0.935*	*0.014*	*-1.682*	*0.047*	*0*
5 to 55°C E(T)(c,e)	0.22	16	0.4337	0.0010	-0.935	0.009	-1.683	0.031	0
5 to 55°C K(1/T)(d,e)	0.22	16	0.4336	0.0005	-0.933	0.010	-1.674	0.033	0
[95OFF/CAP]	0.55						-1.70		-0.0062
5 to 55°C, E(T)(a)	*0.55*	*6*	*0.4675*	*0.0022*	*-0.976*		*-1.704*		*-0.0064*
5 to 55°C E(T)(b)	**0.55**	**14**	**0.4674**	**0.0033**	**-0.976**	**0.022**	**-1.706**	**0.074**	**-0.0061±0.0039**
5 to 55°C, E(T), Cp°(c)	0.55	14	0.4674	0.0034	-0.977	0.022	-1.709	0.073	-0.0062±0.0040
5 to 55°C K(1/T)(d)	0.55	14	0.4673	0.0033	-0.980	0.020	-1.719	0.068	-0.0059±0.0040
5 to 55°C, E(T)(a,e)	*0.55*	*6*	*0.4658*	*0.0019*	*-0.993*	*0.017*	*-1.768*	*0.055*	*0*
5 to 55°C E(T)(c,e)	0.55	14	0.4660	0.0013	-0.994	0.012	-1.771	0.041	0
5 to 55°C K(1/T)(d,e)	0.55	14	0.4660	0.0006	-0.991	0.012	-1.761	0.040	0
[95OFF/CAP]	1						-1.75		-0.0041
5 to 55°C, E(T)(a)	*1*	*6*	*0.5000*	*0.0021*	*-1.027*		*-1.767*		*-0.0048*
5 to 55°C E(T)(b)	**1**	**16**	**0.5001**	**0.0027**	**-1.027**	**0.018**	**-1.766**	**0.060**	**-0.0049±0.0030**
5 to 55°C, E(T), Cp°(c)	1	16	0.5001	0.0027	-1.027	0.018	-1.769	0.059	-0.0050±0.0031
5 to 55°C K(1/T)(d)	1	16	0.5001	0.0027	-1.029	0.016	-1.774	0.055	-0.0050±0.0031
5 to 55°C, E(T)(a,e)	*1*	*6*	*0.4988*	*0.0016*	*-1.040*	*0.013*	*-1.815*	*0.045*	*0*
5 to 55°C E(T)(c,e)	1	16	0.4992	0.0010	-1.042	0.010	-1.821	0.032	0
5 to 55°C K(1/T)(d,e)	1	16	0.4991	0.0005	-1.039	0.010	-1.812	0.033	0
5 to 55°C, E(T)(a)	*1*	*7*	*0.4998*	*0.0023*	*-1.026*		*-1.766*		*-0.0038*
5 to 60°C E(T)(b)	1	18	0.5000	0.0027	-1.026	0.017	-1.764	0.058	-0.0040±0.024
5 to 60°C, E(T), Cp°(c)	1	18	0.5000	0.0028	-1.027	0.017	-1.766	0.057	-0.0041±0.024
5 to 60°C K(1/T)(d)	1	18	0.5000	0.0027	-1.028	0.015	-1.770	0.052	-0.0043±0.024
5 to 60°C, E(T)(a,e)	*1*	*7*	*0.4987*	*0.0007*	*-1.044*	*0.010*	*-1.828*	*0.035*	*0*
5 to 60°C E(T)(c,e)	1	18	0.4991	0.0005	-1.047	0.008	-1.836	0.026	0
5 to 60°C K(1/T)(d,e)	1	18	0.4991	0.0005	-1.044	0.008	-1.829		0
[95OFF/CAP]	1.25						-2.08		0.0090
5 to 55°C, E(T)(a)	*1.25*	*6*	*0.4952*	*0.0094*	*-1.128*		*-2.123*		*0.0117*
5 to 55°C E(T)(b)	**1.25**	**15**	**0.4971**	**0.0101**	**-1.124**	**0.067**	**-2.102**	**0.221**	**0.0083±0.0114**
5 to 55°C, E(T), Cp°(c)	1.25	15	0.4971	0.0102	-1.122	0.066	-2.095	0.219	0.0082±0.0116
5 to 55°C K(1/T)(d)	1.25	15	0.4974	0.0100	-1.115	0.060	-2.072	0.205	0.0065±0.0118
5 to 55°C, E(T)(a,e)	*1.25*	*6*	*0.4984*	*0.0054*	*-1.096*	*0.046*	*-2.005*	*0.154*	*0*
5 to 55°C E(T)(c,e)	1.25	15	0.4988	0.0030	-1.099	0.029	-2.012	0.097	0
5 to 55°C K(1/T)(d,e)	1.25	15	0.4988	0.0015	-1.102	0.029	-2.024	0.096	0
5 to 55°C, E(T)(a)	*1.25*	*7*	*0.4950*	*0.0086*	*-1.128*		*-2.124*		*0.0123*
5 to 60°C E(T)(b)	1.25	17	0.4966	0.0095	-1.123	0.062	-2.101	0.206	0.0096±0.086
5 to 60°C, E(T), Cp°(c)	1.25	17	0.4966	0.0097	-1.121	0.062	-2.093	0.204	0.0096±0.068
5 to 60°C K(1/T)(d)	1.25	17	0.4971	0.0097	-1.112	0.056	-2.061	0.189	0.0085±0.091

Table [95OFF/CAP]-sup (continued)	(M)	n	E (V)	±	$\Delta_r H/F$ (V)	±	$\Delta_r S/F$ (mV.K^{-1})	±	$\Delta_r Cp/(FT°)$ (mV.K^{-2})
5 to 60°C, E(T)$^{(a,e)}$	*1.25*	*7*	*0.4988*	*0.0027*	*-1.073*	*0.038*	*-1.926*	*0.126*	*0*
5 to 60°C E(T)$^{(c,e)}$	1.25	17	0.4991	0.0015	-1.075	0.024	-1.933	0.080	0
5 to 60°C K(1/T)$^{(d,e)}$	1.25	17	0.4992	0.0014	-1.080	0.024	-1.948	0.081	0
[95OFF/CAP]	1.5						-2.04		0.0022
5 to 55°C, E(T)$^{(a)}$	*1.5*	*6*	0.*4989*	*0.0029*	*-1.118*		*-2.075*		*0.0008*
5 to 55°C E(T)$^{(b)}$	**1.5**	**18**	**0.4986**	**0.0045**	**-1.114**	**0.025**	**-2.065**	**0.083**	**0.0011±0.0043**
5 to 55°C, E(T), Cp°$^{(c)}$	1.5	18	0.4986	0.0045	-1.114	0.025	-2.065	0.081	0.0011±0.0044
5 to 55°C K(1/T)$^{(d)}$	1.5	18	0.4987	0.0045	-1.113	0.023	-2.062	0.077	0.0009±0.0045
5 to 55°C, E(T)$^{(a,e)}$	*1.5*	*6*	*0.4991*	*0.0014*	*-1.116*	*0.012*	*-2.068*	*0.040*	*0*
5 to 55°C E(T)$^{(c,e)}$	1.5	18	0.4989	0.0011	-1.111	0.010	-2.054	0.034	0
5 to 55°C K(1/T)$^{(d,e)}$	1.5	18	0.4989	0.0006	-1.112	0.010	-2.055	0.035	0
5 to 55°C, E(T)$^{(a)}$	*1.5*	*7*	*0.4985*	*0.0035*	*-1.117*		*-2.074*		*0.0025*
5 to 60°C E(T)$^{(b)}$	1.5	20	0.4986	0.0044	-1.113	0.024	-2.062	0.080	0.0022±0.0035
5 to 60°C, E(T), Cp°$^{(c)}$	1.5	20	0.4984	0.0045	-1.113	0.024	-2.061	0.079	0.0023±0.0036
5 to 60°C K(1/T)$^{(d)}$	1.5	20	0.4985	0.0045	-1.111	0.021	-2.055	0.073	0.0020±0.0037
5 to 60°C, E(T)$^{(a,e)}$	*1.5*	*7*	*0.4992*	*0.0008*	*-1.105*	*0.011*	*-2.033*	*0.038*	*0*
5 to 60°C E(T)$^{(c,e)}$	1.5	20	0.4990	0.0006	-1.104	0.009	-2.028	0.030	0
5 to 60°C K(1/T)$^{(d,e)}$	1.5	20	0.4990	0.0006	-1.105	0.009	-2.031	0.031	0
[95OFF/CAP]	2						-2.38		0.0132
5 to 55°C, E(T)$^{(a)}$	*2*	*7*	0.5082	0.0069	-1.216		*-2.365*		*0.0131*
5 to 55°C E(T)$^{(b)}$	**2**	**18**	0.5079	0.0076	-1.230	**0.053**	-2.373	**0.176**	**0.0155±0.0091**
5 to 55°C, E(T), Cp°$^{(c)}$	2	18	0.5079	0.0077	-1.228	0.053	-2.423	0.174	0.0157±0.0093
5 to 55°C K(1/T)$^{(d)}$	2	18	0.5080	0.0078	-1.223	0.050	-2.416	0.169	0.0155±0.0098
5 to 55°C, E(T)$^{(a,e)}$	*2*	*7*	0.5119	0.0040	-1.184	0.035	-2.397	0.116	*0*
5 to 55°C E(T)$^{(c,e)}$	2	18	0.5106	0.0026	-1.174	0.026	-2.225	0.086	0
5 to 55°C K(1/T)$^{(d,e)}$	2	18	0.5107	0.0013	-1.180	0.026	-2.246	0.089	0
5 to 60°C, E(T)$^{(a)}$	*2*	*8*	0.5085	0.0067	-1.216		-2.373		*0.0114*
5 to 60°C E(T)$^{(b)}$	2	20	0.5089	0.0076	-1.229	0.051	-2.416	0.168	0.0154±0.0069
5 to 60°C, E(T), Cp°$^{(c)}$	2	20	0.5082	0.0076	-1.227	0.050	-2.412	0.156	0.0136±0.0071
5 to 60°C K(1/T)$^{(d)}$	2	20	0.5082	0.0076	-1.223	0.047	-2.398	0.160	0.0141±0.0076
5 to 60°C, E(T)$^{(a,e)}$	*2*	*8*	0.5123	0.0019	-1.169	0.028	-2.202	0.093	*0*
5 to 60°C E(T)$^{(c,e)}$	2	20	0.5106	0.0013	-1.157	0.021	-2.168	0.072	0
5 to 60°C K(1/T)$^{(d,e)}$	2	20	0.5108	0.0013	-1.163	0.023	-2.189	0.076	0

(a) The experimental data of the table [95OFF/CAP]-1 (i.e. the E mean value for each chemical condition) are fitted to the following equation: $E(T,I) \approx E(T°,I) + (t-25)\, \Delta_r S°(T°,I) / F + (t-25)^2\, \Delta_r Cp(T°,I) / (2\, F\, T°)$, where T° = 298.15 K, between 5 and 55 or 60°C (as indicated in the first column).

(b) The fitting results are obtained with the same procedure as above(a), but from all the data (instead of the E mean value for each chemical condition).

(c) The fitting results are obtained with similar procedure as above(b); but by using the following classical equation: $E(T,I) \approx E(T°,I) + (t-25)\, \Delta_r S°(T°,I) / F + (T-T° - T \ln(T/T°))\, \Delta_r Cp(T°,I) / F$, obtained assuming constant Cp.

(d) $\log_{10}K$ (= F E /(R T ln10) calculated from the experimental data, E) data are fitted to the following equation: $\log_{10}K(T,I) \approx \log_{10}K(T°,I) - (1/T - 1/T°)\, \Delta_r H°(T°,I) / (R \ln 10) + (1/T - 1/T°)^2\, T°^2\, \Delta_r Cp(T°,I) / (2\, R \ln 10)$, between 5 and 55 or 60°C (as indicated in the first column).

(e) $\Delta_r Cp = 0$ is fixed, curve fitting is then linear regression of the experimental data E$^{(a,b,c)}$ (or $\log_{10}K^{(d)}$) as a function of (t-25)$^{(a,b,c)}$ or (1/T - 1/298.15)$^{(d)}$.

Table [95OFF/CAP]-sup *(continued)*: These values can be deduced from the above part of the table by using classical thermodynamic equations. Footnotes have the same meaning as above.

			$\Delta_r G$ kJ.mol.$^{-1}$	±	$\Delta_r H$ kJ.mol.$^{-1}$	±	$\Delta_r S$ J.mol.$^{-1}$K^{-1}	±	$\Delta_r Cp$ J.mol.$^{-1}$K^{-1}	$\log_{10}K$	±
5 to 55°C, E(T)$^{(a)}$	*0*	*6*	*-32.807*	*0.166*	*-88.93*		*-188.2*		*-704*	*-5.748*	*0.029*
5 to 55°C E(T)$^{(b)}$	**0**	**6**	**-32.830**	**0.224**	**-88.77**		**-187.6**		**-759**	**-5.751**	**0.039**
5 to 55°C, E(T), Cp°$^{(c)}$	0	6	-32.833	0.224	-88.96		-188.3		-770	-5.752	0.039
5 to 55°C K(1/T)$^{(d)}$	0	6	-32.782	0.253	-89.41		-189.9		-779	5.743	0.044
5 to 55°C, E(T)$^{(a,e)}$	*0*	*6*	*-32.493*	*0.311*	*-92.14*	*2.67*	*-200.1*	*8.9*	*0*	*-5.692*	*0.054*
5 to 55°C E(T)$^{(c,e)}$	0	6	-32.490	0.341	-92.22	2.93	-200.3	9.8	0	-5.692	0.060
5 to 55°C K(1/T)$^{(d,e)}$	0	6	-32.482	0.169	-91.68	2.95	-198.6	9.9	0	5.691	0.030
5 to 55°C, E(T)$^{(a)}$	*0*	*7*	*-32.414*	*2.383*	*-88.25*		*-187.3*		*376*	*-5.679*	*0.417*
5 to 60°C E(T)$^{(b)}$	0	7	-32.383	1.466	-88.15		-187.0		325	-5.673	0.257
5 to 60°C, E(T), Cp°$^{(c)}$	0	7	-32.432	2.428	-87.89		-186.0		340	-5.682	0.425
5 to 60°C K(1/T)$^{(d)}$	0	7	-32.799	0.203	-89.72		-190.9		-845	5.746	0.036
5 to 60°C, E(T)$^{(a,e)}$	*0*	*7*	*-32.601*	*0.356*	*-85.40*	*5.03*	*-177.1*	*16.8*	*0*	*-5.711*	*0.062*
5 to 60°C E(T)$^{(c,e)}$	0	7	-32.600	0.363	-85.44	5.14	-177.2	17.2	0	-5.711	0.064
5 to 60°C K(1/T)$^{(d,e)}$	0	7	-32.551	0.315	-85.89	4.75	-178.9	16.0	0	5.703	0.055

Table [95OFF/CAP]-sup ***(continued)***			Δ_rG kJ.mol.$^{-1}$	±	Δ_rH kJ.mol.$^{-1}$	±	Δ_rS J.mol.$^{-1}$K^{-1}	±	Δ_rCp J.mol.$^{-1}$K^{-1}	$\log_{10}K$	±
5 to 55°C, E(T)(a)	*0.22*	*6*	*-41.971*	*0.153*	*-88.72*		*-156.8*		*-328*	*-7.353*	*0.027*
5 to 55°C E(T)(b)	**0.22**	**16**	**-41.952**	**0.257**	**-88.73**		**-156.9**		**-304**	**-7.350**	**0.045**
5 to 55°C, E(T), Cp°(c)	0.22	16	-41.951	0.256	-88.80		-157.1		-306	-7.349	0.045
5 to 55°C K(1/T)(d)	0.22	16	-41.954	0.255	-88.93		-157.6		-318	7.350	0.045
5 to 55°C, E(T)(a,e)	*0.22*	*6*	*-41.824*	*0.157*	*-90.21*	*1.35*	*-162.3*	*4.5*	*0*	*-7.327*	*0.027*
5 to 55°C E(T)(c,e)	0.22	16	-41.844	0.096	-90.25	0.91	-162.4	3.0	0	-7.331	0.017
5 to 55°C K(1/T)(d,e)	0.22	16	-41.841	0.049	-90.00	0.94	-161.5	3.1	0	7.330	0.009
5 to 55°C, E(T)(a)	*0.55*	*6*	*-45.106*	*0.213*	*-94.13*		*-164.4*		*-366*	*-7.902*	*0.037*
5 to 55°C E(T)(b)	**0.55**	**14**	**-45.095**	**0.322**	**-94.16**		**-164.6**		**-352**	**-7.900**	**0.056**
5 to 55°C, E(T), Cp°(c)	0.55	14	-45.095	0.324	-94.26		-164.9		-354	-7.900	0.057
5 to 55°C K(1/T)(d)	0.55	14	-45.088	0.320	-94.53		-165.8		-339	7.899	0.056
5 to 55°C, E(T)(a,e)	*0.55*	*6*	*-44.943*	*0.186*	*-95.80*	*1.60*	*-170.6*	*5.3*	*0*	*-7.874*	*0.033*
5 to 55°C E(T)(c,e)	0.55	14	-44.961	0.127	-95.90	1.18	-170.9	3.9	0	-7.877	0.022
5 to 55°C K(1/T)(d,e)	0.55	14	-44.958	0.061	-95.62	1.16	-169.9	3.9	0	7.876	0.011
5 to 55°C, E(T)(a)	*1*	*6*	*-48.247*	*0.198*	*-99.07*		*-170.5*		*-275*	*-8.453*	*0.035*
5 to 55°C E(T)(b)	**1**	**16**	**-48.253**	**0.265**	**-99.06**		**-170.4**		**-282**	**-8.454**	**0.046**
5 to 55°C, E(T), Cp°(c)	1	16	-48.254	0.265	-99.13		-170.6		-285	-8.454	0.046
5 to 55°C K(1/T)(d)	1	16	-48.255	0.259	-99.29		-171.2		-289	8.454	0.045
5 to 55°C, E(T)(a,e)	*1*	*6*	*-48.125*	*0.150*	*-100.32*	*1.30*	*-175.1*	*4.3*	*0*	*-8.431*	*0.026*
5 to 55°C E(T)(c,e)	1	16	-48.161	0.094	-100.53	0.93	-175.7	3.1	0	-8.437	0.016
5 to 55°C K(1/T)(d,e)	1	16	-48.158	0.047	-100.28	0.94	-174.8	3.2	0	8.437	0.008
5 to 55°C, E(T)(a)	*1*	*7*	-48.227	0.219	-99.02		-170.4		-220	-8.449	0.038
5 to 60°C E(T)(b)	1	18	-48.247	0.259	-98.99		-170.2		-232	-8.453	0.045
5 to 60°C, E(T), Cp°(c)	1	18	-48.242	0.271	-99.05		-170.4		-237	-8.452	0.047
5 to 60°C K(1/T)(d)	1	18	-48.245	0.258	-99.16		-170.8		-249	8.452	0.045
5 to 60°C, E(T)(a,e)	*1*	*7*	*-48.118*	*0.070*	*-100.71*	*1.00*	*-176.4*	*3.3*	*0*	*-8.430*	*0.012*
5 to 60°C E(T)(c,e)	1	18	-48.156	0.046	-100.98	0.74	-177.2	2.5	0	-8.436	0.008
5 to 60°C K(1/T)(d,e)	1	18	-48.151	0.045	-100.75	0.76	-176.4	2.6	0	8.436	0.008
5 to 55°C, E(T)(a)	*1.25*	*6*	*-47.784*	*0.903*	*-108.85*		*-204.8*		*675*	*-8.371*	*0.158*
5 to 55°C E(T)(b)	**1.25**	**15**	**-47.958**	**0.976**	**-108.42**		**-202.8**		**475**	**-8.402**	**0.171**
5 to 55°C, E(T), Cp°(c)	1.25	15	-47.961	0.980	-108.24		-202.2		469	-8.402	0.172
5 to 55°C K(1/T)(d)	1.25	15	-47.996	0.965	-107.61		-200.0		374	8.409	0.169
5 to 55°C, E(T)(a,e)	*1.25*	*6*	*-48.086*	*0.517*	*-105.78*	*4.45*	*-193.5*	*14.8*	*0*	*-8.424*	*0.091*
5 to 55°C E(T)(c,e)	1.25	15	-48.125	0.292	-106.00	2.81	-194.1	9.4	0	-8.431	0.051
5 to 55°C K(1/T)(d,e)	1.25	15	-48.130	0.141	-106.36	2.75	-195.3	9.3	0	8.432	0.025
5 to 55°C, E(T)(a)	*1.25*	*7*	*-47.762*	*0.826*	*-108.87*		*-204.9*		*710*	*-8.367*	*0.145*
5 to 60°C E(T)(b)	1.25	17	-47.915	0.918	-108.36		-202.7		551	-8.394	0.161
5 to 60°C, E(T), Cp°(c)	1.25	17	-47.917	0.934	-108.14		-202.0		552	-8.395	0.164
5 to 60°C K(1/T)(d)	1.25	17	-47.967	0.933	-107.27		-198.9		489	8.403	0.163
5 to 60°C, E(T)(a,e)	*1.25*	*7*	*-48.122*	*0.258*	*-103.52*	*3.65*	*-185.8*	*12.2*	*0*	*-8.431*	*0.045*
5 to 60°C E(T)(c,e)	1.25	17	-48.153	0.148	-103.75	2.31	-186.5	7.7	0	-8.436	0.026
5 to 60°C K(1/T)(d,e)	1.25	17	-48.164	0.140	-104.21	2.32	-188.0	7.8	0	8.438	0.024
5 to 55°C, E(T)(a)	*1.5*	*6*	*-48.133*	*0.278*	*-107.84*		*-200.2*		*45*	*-8.433*	*0.049*
5 to 55°C E(T)(b)	**1.5**	**18**	**-48.109**	**0.436**	**-107.53**		**-199.3**		**64**	**-8.428**	**0.076**
5 to 55°C, E(T), Cp°(c)	1.5	18	-48.109	0.436	-107.50		-199.2		64	-8.428	0.076
5 to 55°C K(1/T)(d)	1.5	18	-48.115	0.433	-107.42		-198.9		51	8.429	0.076
5 to 55°C, E(T)(a,e)	*1.5*	*6*	*-48.153*	*0.134*	*-107.63*	*1.15*	*-199.5*	*3.8*	*0*	*-8.436*	*0.023*
5 to 55°C E(T)(c,e)	1.5	18	-48.135	0.111	-107.22	1.00	-198.2	3.3	0	-8.433	0.019
5 to 55°C K(1/T)(d,e)	1.5	18	-48.136	0.055	-107.27	1.01	-198.3	3.4	0	8.433	0.010
5 to 55°C, E(T)(a)	*1.5*	*7*	*-48.096*	*0.339*	*-107.76*		*-200.1*		*146*	*-8.426*	*0.059*
5 to 60°C E(T)(b)	1.5	20	-48.109	0.425	-107.42		-198.9		129	-8.428	0.074
5 to 60°C, E(T), Cp°(c)	1.5	20	-48.089	0.439	-107.39		-198.9		130	-8.425	0.077
5 to 60°C K(1/T)(d)	1.5	20	-48.096	0.433	-107.21		-198.3		117	8.426	0.076
5 to 60°C, E(T)(a,e)	*1.5*	*7*	*-48.169*	*0.077*	*-106.66*	*1.09*	*-196.2*	*3.6*	*0*	*-8.439*	*0.013*
5 to 60°C E(T)(c,e)	1.5	20	-48.146	0.056	-106.48	0.86	-195.6	2.9	0	-8.435	0.010
5 to 60°C K(1/T)(d,e)	1.5	20	-48.149	0.054	-106.59	0.88	-196.0	3.0	0	8.435	0.010
5 to 55°C, E(T)(a)	*2*	*7*	*-49.032*	*0.670*	*-117.29*		*-228.9*		*753*	*-8.590*	*0.117*
5 to 55°C E(T)(b)	**2**	**18**	**-49.006**	**0.738**	**-118.71**		**-233.8**		**891**	**-8.586**	**0.129**
5 to 55°C, E(T), Cp°(c)	2	18	-49.005	0.740	-118.52		-233.1		902	-8.585	0.130
5 to 55°C K(1/T)(d)	2	18	-49.010	0.757	-117.98		-231.3		892	8.586	0.133
5 to 55°C, E(T)(a,e)	*2*	*7*	*-49.391*	*0.382*	*-114.22*	*3.36*	*-217.4*	*11.2*	*0*	*-8.653*	*0.067*
5 to 55°C E(T)(c,e)	2	18	-49.262	0.255	-113.27	2.48	-214.7	8.3	0	-8.630	0.045
5 to 55°C K(1/T)(d,e)	2	18	-49.274	0.128	-113.89	2.55	-216.7	8.6	0	8.632	0.022

Table [95OFF/CAP]-sup ***(continued)***			Δ_rG kJ.mol.$^{-1}$	±	Δ_rH kJ.mol.$^{-1}$	±	Δ_rS J.mol.$^{-1}$K^{-1}	±	Δ_rCp J.mol.$^{-1}$K^{-1}	$\log_{10}K$	±
5 to 60°C, E(T)$^{(a)}$	*2*	*8*	*-49.066*	*0.649*	*-117.34*		*-229.0*		*659*	*-8.596*	*0.114*
5 to 60°C E(T)$^{(b)}$	2	20	-49.100	0.732	-118.59		-233.1		888	-8.602	0.128
5 to 60°C, E(T), Cp°$^{(c)}$	2	20	-49.036	0.730	-118.43		-232.7		784	-8.591	0.128
5 to 60°C K(1/T)$^{(d)}$	2	20	-49.031	0.730	-118.03		-231.4		809	8.590	0.128
5 to 60°C, E(T)$^{(a,e)}$	*2*	*8*	*-49.426*	*0.184*	*-112.76*	*2.69*	*-212.4*	*9.0*	*0*	*-8.659*	*0.032*
5 to 60°C E(T)$^{(c,e)}$	2	20	-49.270	0.128	-111.63	2.07	-209.2	6.9	0	-8.632	0.022
5 to 60°C K(1/T)$^{(d,e)}$	2	20	-49.287	0.126	-112.25	2.17	-211.2	7.3	0	8.635	0.022

See footnotes at the end of the previous part of this table.

Table [97VIT/CAP])-sup: Np(VI) solubility in bicarbonate/carbonate aqueous solutions at room temperature. Horizontal lines separate different batches.

$\log_{10}[CO_3^{-2}]$	$\log_{10}[Np(VI)]_t$		$\log_{10}[CO_3^{-2}]$	$\log_{10}[Np(VI)]_t$	
-9.7	-4.24	3 M $NaClO_4$, P_{CO_2} 1atm, 17days	-4.2	-3.18	0.5 M $NaClO_4$
-9.7	-4.25	3 M $NaClO_4$, P_{CO_2} 1atm, 17.5 days	-4.35	-3	0.5 M $NaClO_4$
-9.5	-4.24	3 M $NaClO_4$, P_{CO_2} 1atm, 18 days	-4.62	-3.7	0.5 M $NaClO_4$
-5.6	-3.95	3 M $NaClO_4$	-4.82	-3.9	0.5 M $NaClO_4$
-6.36	-4.34	3 M $NaClO_4$	-4.72	-3.4	0.17 M $NaClO_4$
-6.28	-4.41	3 M $NaClO_4$, 4 days later	-4.72	-3.92	0.17 M $NaClO_4$
-6.82	-4.80	3 M $NaClO_4$	-4.8	-3.7	0.17 M $NaClO_4$
-2.95	-3.08	3 M $NaClO_4$	-4.82	-3.72	0.17 M $NaClO_4$
-3.1	-3.40	3 M $NaClO_4$			
-3.42	-3.63	3 M $NaClO_4$			