Neptunium en solution carbonate concentrée réductrice : bibliographie pour l'OCDE-AEN-TDB.

Pierre Vitorge.pierre.vitorge(a)cea.fr

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RESUME

Dans les eaux naturelles Np(IV) ne devrait pas être complexé par les carbonates (Rai et Ryan 1985). En milieu carbonate concentré, par contre, Np(IV) est complexé ; mais il n'existe aucune stoechiométrie prouvée, ni aucune donnée thermodynamique validée. Certains auteurs utilisent encore des valeurs publiées fausses qui elles, induisent pour des eaux naturelles, la prévision de la formation majoritaire de complexes carbonate et ainsi des solubilités surestimées de plusieurs ordres de grandeur. Les résultats expérimentaux publiés sont compatibles avec l'analogie U-Np-Pu. La revue de la TDB déjà publiée sur l'uranium (Grenthe et al. 1992) a retenu la formation majoritaire de $U(CO_3)_4^{4-}$ et $U(CO_3)_5^{6-}$ en milieu carbonate concentré. Des mesures spectrophotométriques et électrochimiques relativement classiques (mais bien conçues) devraient permettre de vérifier expérimentalement les interprétations proposées. La préparation de Np(III) s'accompagne de réduction de l'eau dans ce milieu, ce qui limite les possibilités de mesure de la stabilité de ses complexes. Des données (non encore publiées) sont brièvement fournies sans examen critique, en milieu carbonate concentré en fonction de la force ionique sur la dissociation du complexe limite de Np(IV), sur le couple Np(V)/Np(IV) et aussi en fonction de la température sur Np(VI)/Np(V).

SUMMARY

There is no evidence of any Np(IV) carbonate complex in natural waters (Rai et Ryan 1985). Np(IV) complexes are formed in concentrated carbonate media; but their published stoechiometry and stability are very questionable. Some authors are still using incorrect published values, that induce solubility overestimated by several orders of magnitude. U-Np-Pu analogy is consistent with all the published experimental results. The TDB review on uranium (Grenthe et al. 1992) has selected $U(CO_3)_4^{4-}$ and $U(CO_3)_5^{6-}$ to be the major species in concentrated carbonate media. Classical spectrophotometric and electrochemical techniques (but using correct methodology) might be enough to check the proposed interpretation. Water is reduced during the Np(III) preparation in these conditions. This is an important limitation to measure the stability of its complexes. Unpublished results are given without any reviewing, in concentrated carbonate media at different ionic strengthes for the dissociation of the limiting complex of Np(IV), the Np(V)/Np(IV) redox couple, and also at different temperatures for the Np(VI)/Np(V) redox couple.

SOMMAIRE

1. Introduction

Nous avons passé en revue la chimie de Np(IV) et Np(III) en milieu carbonate. Cette revue est en cours de comparaison avec celle effectuée sur le plutonium par Ullman et Sullivan. Nous donnons ici le texte élaboré pour la TDB (Thermodynamic Data Base de l'AEN OCDE) qui fera partie de l'appendix A du volume Chemical thermodynamics of neptunium and plutonium (en anglais). Les notations et méthodologies sont celles adoptées dans la TDB et publiées [92GRE/FUG]. **La publication de la présente note a notamment pour objectif de servir de support de discussion aux auteurs des publications citées pour que je prenne en compte leur avis dès maintenant**[1]**.** Cette appendix est le résultat de l'analyse de chaque publication. La synthèse fait l'objet d'un chapitre déjà transmis à l'OCDE; mais que nous avons l'intention de réécrire de façon plus concise. De cette analyse il ressort actuellement :

a) La solubilité du neptunium est de 5 nanomoles par litre en milieu réducteur peu acide tant que la concentration totale en carbonate reste inférieure à 10 millimoles par litre. Toutefois cette valeur pourrait n'être que la limite de sensibilité des méthodes classiques d'analyse. Les solubilités de U(IV) et Pu(IV) dans ces conditions sont plutôt de l'ordre de 0,1 à 0,3 nanomole par litre. Outre la nécessité d'améliorer d'un facteur 10 au moins la limite de sensibilité, la mesure de la solubilité de Np(IV) présente des difficultés particulières de préparation et de caractérisation de la solution et du solide. Ces difficultés sont expliquées dans la revue bibliographique ci-après.
b) Les résultats publiés sur Np(IV), confirment l'analogie entre U, Np et Pu en milieu carbonate concentré. Il existe au moins deux complexes carbonate de Np(IV) en milieu carbonate concentré ; mais aucune publication, même après réinterprétation, ne permet d'en déterminer la stoechiométrie ou la stabilité. Les expériences publiées montrent que des études électrochimiques et spectrophotométriques supplémentaires relativement classiques devraient permettent de conclure ou du moins y contribuer. L'analyse ci-après des publications précise cette appréciation et les modes opératoires corrects ou, au contraire, à éviter.

Quelques vérifications expérimentales nous ont permis par ailleurs de confirmer nos appréciations (développées dans cette revue, § 2) et donc de comprendre pourquoi les publications ne peuvent être actuellement que partiellement interprétées. La confirmation porte sur (DEA RRR, IPN Orsay, de Lætitia Delmau que nous publierons en NT CEA [95DEL] pour ensuite l'examiner dans le cadre de la TDB) :

* la façon de préparer le complexe carbonate limite de Np(IV) [71MOS5] [79FED/PER] [81WES/SUL],
  - sa caractérisation par son spectre d'absorption [71MOS5] [77SAI/UEN] [81WES/SUL] [93LI/KAT],
  - sa stabilité [85RAI/RYA] [93LI/KAT] analogue à celle de U [92GRE/FUG] et Pu [92CAP],

* le spectre d'absorption du complexe dissocié [93LI/KAT],

* l'ordre de grandeur de la valeur du potentiel d'oxydo-réduction du couple Np(V)/Np(IV) [79FED/PER].

Les calculs (en cours donc) tirés de [95DEL] confirment qualitativement les conclusions du présent rapport ; toutefois le domaine d'existence du complexe limite carbonate de Np(IV) est très sensible à la force ionique ce qui pourrait éventuellement changer les valeurs numériques finales proposées ici, ainsi que la discussion sur certaines études spectrophotométriques [77SAI/UEN] [81WES/SUL].

Comme il y a trop peu de résultats expérimentaux publiés, nous suggérons les mesures suivantes. Les premières vérifications expérimentales évoquées ci-dessus pourraient être étendues à des mesures systématiques en contrôlant correctement les principaux paramètres (ici potentiel de jonction, pH et son étalonnage, force ionique et concentration totale en carbonate). On pourrait ensuite avec relativement peu d'efforts supplémentaires mesurer l'influence de la température. Ce type de mesure présente de réelles difficultés qui peuvent limiter la précision et donc la validation des stoechiométries proposées. Une façon relativement simple de confirmer la démarche consisterait à comparer des analogues chimiques notamment ceux avec lesquels on peut atteindre des conditions chimiques accessibles différentes de celles accessibles pour le Np(IV). Il existe des données plus ou moins bien interprétées (citées dans la revue ci-après), ou il est possible d'en mesurer en milieux carbonate sur Ce(IV) [72DER] [73DER/FAU2] [73DER/FAU3] [77VOL/FRO] [90HAL/FOU], Th(IV) [72DER] [73DER/FAU2] [73DER/FAU3] [77VOL/FRO] [87JOA/BIG], U(IV)

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[1] **The present report should now be discussed by the author of the publications, that I have reviewed.**

[92GRE/FUG], Pu(IV), Am(IV) [83BOU/GUI] [87ROB] sur les couples Ce(IV)/Ce(III), Am(IV)/Am(III), U(VI)/U(IV), Pu(VI)/Pu(IV), Pu(V)/Pu(IV) et sur les dismutations de Pu(V) et d'Am(V).

Le travail pour la TDB continue sur le neptunium aux autres degrés d'oxydation.

Par ailleurs, l'utilisation de nos données chimiques, continue avec notamment la sorption de Np(V) (thèse de Laure Gorgeon dirigée par Jacques Ly, 25 novembre 1994, Université Paris 6, France) sur des argiles et le couplage avec la migration : modélisation et validation expérimentale (thèse de France Lefèvre dirigée par Michel Sardin à soutenir, en principe en 1995, Nancy, France).

Ce travail a été utilisé pour un exposé aux *25èmes Journées des Actinides L'Aquila, Italie, 7-11 avril 1995 (Actinide(IV) in carbonate media, Pierre Vitorge, Lætitia Delmau, Hélène Capdevila).*

Remerciements

Ce travail bénéficie de calculs d'Hélène Capdevila sur la spectrophotométrie de Pu(IV) à partir des résultats expérimentaux de sa thèse [92CAP] et sur Np(IV) à partir de ceux du stage de DEA de Lætitia Delmau. Ce travail reprend également les autres résultats du stage de DEA de Lætitia Delmau. Patrick Tran Thé a scanné des figures publiées pour obtenir des valeurs numériques de points expérimentaux et pour comparer les spectres de Np(IV) en milieu carbonate concentré. Najiba Benjelloun, Professeur invitée de l'Université de Casablanca (Maroc), a participé à ce travail. Il est en partie financé par l'ANDRA.

2. Np(IV) carbonate complexes, discussion of publications. Appendix A

Draft of a part of the Appendix A of Chemical thermodynamics of neptunium and plutonium (to be edited by the Nuclear Energy Agency -OECD-), by Pierre Vitorge for reviewing within the TDB Np/Pu specialist team.

2.1. [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(IV) was measured in 0.15 to 2.20 M $(NH_4)_2CO_3$ aqueous solutions (figure [71MOS5]-4), together with the absorption spectrum of one of these solutions. The pH was measured (figure [71MOS5]-1). This is the first experimental work, that proposes a formation constant of a Np(IV) soluble complex in concentrated carbonate media. It has then been extensively cited and used. Unfortunately Rai and Ryan [85RAI/RYA] later pointed out many reasons to conclude, that the interpretation of the experiments is "completely erroneous", and the present review agrees with Rai and Ryan (see below). Even after these comments, Moskvin's interpretation and number are still used. For this reason we could not simply ignore Moskvin's work, and we insist again on the inconsistency of Moskvin's interpretation. Let us first remind a few qualitative aspects of the actinide(IV) chemistry, that were known before this Moskvin's work (and partially used by him):

a To study Pu(IV) in carbonate solutions (or to prepare solid Pu(IV) carbonates) one should not mixed an acidic Pu^{4+} solution with a carbonate one, because this leads to the non reversible formation of polymeric Pu(IV) hydroxide. This is certainly also the case to a certain extend, for Np(IV) and other actinide(IV).

b One (at least) strong complex explains the high solubility of actinide(IV) in concentrated carbonate solutions.

c Solid phases of lanthanide or actinide(IV) containing carbonates and cations, M^+, are formed in contact with some carbonate or bicarbonate aqueous solutions; one of them is possibly $M_6Pu(CO_3)_5.xH_2O$; other ones (with other stoichiometry) might as well be formed.

Later works also confirmed this knowledge, typically:

d The dissolution of the Pu(IV) oxide is very slow, except when a chemical can directly react at his surface. It can be a strong reducing, oxidising or complexing agent. This is certainly due to some specific strong Pu-O bond, that probably also forms in solid hydroxide when ageing, and in the polymeric hydroxide.

e The following lanthanide and actinide(IV) solid carbonates have been characterised: $Na_6Ce(CO_3)_5.12H_2O$ [75VOL/RIM4], $Na_6Th(CO_3)_5.12H_2O$ [75VOL/RIM3] [88MAR/HER], $Na_4Ce(CO_3)_4.7H_2O$ [73DER/FAU1]. The structure, many infrared studies of these solids, and other results indicate that (An or Ln)$(CO_3)_5^{6-}$ is probably a very stable anion, where the five CO_3^{2-} ligands are bidentate in the M_6(An or Ln)$(CO_3)_5.12H_2O$ solids. This highly charged anion is precipitated out or stabilised by various cations, specially big ones [75VOL/RIM1] [75VOL/RIM2], that certainly lower the repulsion between them. The present review on uranium [92GRE/FUG] considered that "the composition of the limiting complex $U(CO_3)_5^{6-}$ [is] well established". Cations probably also stabilise them in solutions through ion pairing, and this affects the specific interaction coefficient.

Still, (Ce or Th)$(CO_3)_6^{8-}$ are also proposed in solution [73DER/FAU2] [73DER/FAU3] and recently determined in the $Na_6BaTh(CO_3)_6.6H_2O$ solid compound [90YAM/PUS].

2.1.1.pH and speciation

There are no details about the calibration of the pH electrode. The medium is quite buffered (see below); but the exact pH cannot be calculated, because the gas exchanges are not known. Still, we calculate it with the equilibrium constants selected in this review. The major anions are CO_3^{2-}, HCO_3^- and OH^-, we then avoid to use explicitly the specific interaction coefficients between these anions and the reactive cations, typically Np^{4+} and H^+. For this we are using $\log_{10}[OH^-]$ instead of pH and $\beta'_5 = m_{Np(CO_3)_5^{6-}} / a_{Np^{4+}} /(m_{CO_3^{2-}})^5$ instead of $\beta_5 = m_{Np(CO_3)_5^{6-}} / m_{Np^{4+}} /(m_{CO_3^{2-}})^5$. β'_5 and β_5 have the same standard value, $\beta_5°$: only ionic strength corrections are different. We use some approximations (tables [71MOS5]-1) for the unknown specific

Table [71MOS5]-1a Specific interaction coefficients used to calculate the speciation in the Moskvin's work [71MOS5] on Np solubility in $(NH_4)_2CO_3$ solutions. The H_2O value is used to estimate the activity of water, a_{H_2O}, assuming that $\log_{10}(a_{H_2O}) \approx -0{,}0142\ m_{(NH_4)_2CO_3}$. For comparison, the values used to interpret other publications, in this appendix, are also tabulated.

	$(NH_4)_2CO_3$	Na_2CO_3	K_2CO_3	$NaHCO_3$
H_2O	-0.0142	-0.0191	-0.0193	-0.0135
OH^-	0.09	0.0495	0.09	0.0495
CO_3^{2-}	-0.02	-0.0697	-0.02	-0.0697
HCO_3^-	-0.02	0.0019	-0.02	0.0019

Table [71MOS5]-1b Equilibrium constants, K°, and specific interaction coefficient differences, Δε', used to calculate the speciation in the Moskvin's work [71MOS5] on Np solubility in $(NH_4)_2CO_3$ solutions. The contribution of the activity of water is included in Δε', (see table [71MOS5]-1a). lg is $\log_{10}$. We use concentration in molal units for calculation except for H^+: h is its activity. $^*CO_2$ represent CO_2 or H_2CO_3. Δε' values used to interpret other publications, in this appendix, are also tabulated.

Name	Equilibrium	lg K°	Δε' $(NH_4)_2CO_3$	Δε' Na_2CO_3	Δε' K_2CO_3	Δε' $NaHCO_3$
k_e	$m_{OH^-}\ h/a_{H_2O}$	-14.00	0.1042	0.0686	0.1093	0.063
K_1	$m_{NH_4^+}\ m_{OH^-}\ /a_{H_2O}\ m_{NH_3}$	-4.75	0.0842			
k_1	$m_{OH^-}\ m_{HCO_3^-}/(m_{CO_3^{2-}}\ a_{H_2O})$	-3.67	0.1042	0.1402	0.1093	0.1346
$k_{1,2}$	$m_{OH^-}\ m_{*CO_2}/m_{HCO_3^-}$	-7.65	0.11	0.0476	0.11	0.0476
k_{p1}	$m_{OH^-}\ P_{CO_2}/m_{HCO_3^-}$	-6.18	0.11	0.0476	0.11	0.0476
	$m_{NH_4^+}\ /(m_{NH_3}\ h)$	9.25	-0.02			
	$m_{HCO_3^-}/(h\ m_{CO_3^{2-}})$	10.33	0	0.0716	0	0.0716
	$m_{*CO_2}\ a_{H_2O}\ /(h^2\ m_{CO_3^{2-}})$	16.68	0.0058	0.0506	0.0007	0.0562
	$P_{CO_2} a_{H_2O}\ /(h^2\ m_{CO_3^{2-}})$	18.15	0.0058	0.0506	0.0007	0.0562
	$^*CO_2\ a_{H_2O}\ /(m_{HCO_3^-}\ h)$	6.35	0.0058	-0.021	0.0007	-0.0154
	P_{CO_2}/m_{*CO_2}	1.47	0	0	0	0
	$P_{CO_2} a_{H_2O}/(m_{HCO_3^-}\ h)$	7.82	0.0058	-0.021	0.0007	-0.0154

interaction coefficients. We calculate the molality-molarity conversions with the following approximation: $\log_{10}$Molarity ≈ $\log_{10}$m - 0.0155 m, where m is the $(NH_4)_2CO_3$ molality.

This type of approximations was tested on Na_2CO_3 and K_2CO_3 solutions. As expected (figure [71MOS5]-1), the pH has a constant value (table [71MOS5]-1c): this is due to the mixing of the weak base, CO_3^{2-}, with the weak acid, NH_4^+, that are both coming from the solid, $(NH_4)_2CO_3$. The variations of the (calculated) pH are only due to the ionic strength effects (on the equilibrium constant of the acid-base equilibrium). The calculated partial pressure in "closed system" (neglecting the gas exchange between the solution and the air above it) is higher than the atmospheric pressure (table [71MOS5]-1c). As equilibrating with the air, carbonic gas comes then out of the previous "closed system", that will also lose some ammoniac gas. It then loses some acid (carbonic gas) and some base (ammoniac gas), this should not much affect the pH; but the ionic strength should also vary. There is up to 0.6 unit between the pH values measured by Moskvin and the ones that we are calculating (figure [71MOS5]-1). The measured pH also varied too much as a function of $[(NH_4)_2CO_3]$: this is certainly due to the liquid junction variations. This can also explain the 0.6 unit shift. Two limiting cases are shown in the figure [71MOS5]-1, and in the table [71MOS5]-1c, the lost of ammoniac gas (it is a base) should lower the pH calculated for the open system, that is then closest to the unknown pH than the calculated one: the system is quite buffered. Moskvin's pH values increase with $[(NH_4)_2CO_3]$: this increase can be due to the above artefact (liquid junction and electrode calibration). At least (see below) for this reason Moskvin's interpretation of his soluble complex is not reliable. The artefact might also be due to some uncontrolled exchange between the working solutions and the air, or due to some other part of the experimental procedure, that is not much described.

2.1.2.Spectrophotometry

Moskvin reports the absorption spectrum of the supernatant of the 1.5 M $(NH_4)_2CO_3$ solution, where he measured a solubility of 0.0174 M of Np(IV). The Np(IV) and Np(VI) solubility's measured by Moskvin in similar conditions are of the same order of magnitude; but neither Np(V), nor Np(VI) can be detected in this spectrum, and it can be attributed to Np(IV). It has been confirmed later [77SAI/UEN] [81WES/SUL] [84VAR/HOB] [93LIT/KAT] [95DEL], except around 500 nm and lower, where the base line of the spectrum reported by Moskvin, rises up. This can reasonably be attributed to the effect of small particles of solid in

Table [71MOS5]-1c Speciation in $(NH_4)_2CO_3$ solutions, calculated with the parameters of the tables [71MOS5]-1a and b. M is the initial concentration of $(NH_4)_2CO_3$. lg is $\log_{10}$. The definitions of the constants are in table [71MOS5]-1b (name); but they are here in molar (and not molal) units. For each M value the speciation is calculated for a closed system (upper part of the table) and (lower part of the table) a system where the carbonic gas is equilibrated with the air ($\lg P_{CO_2} = -3.5$).

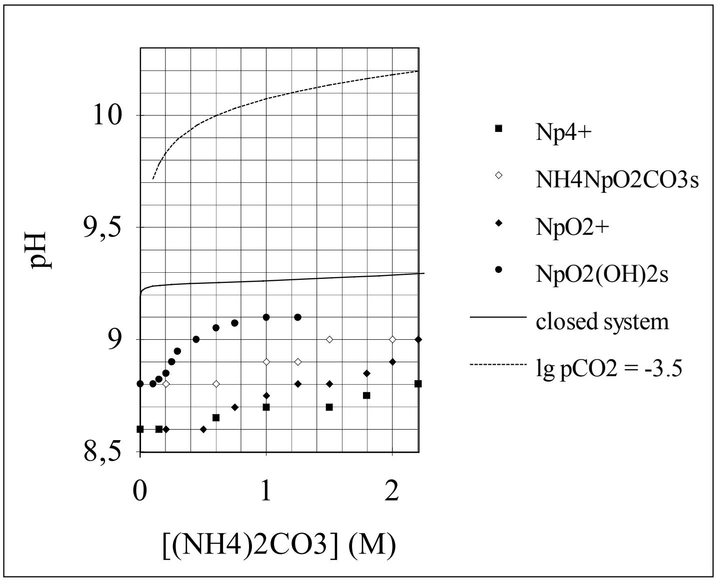
M	$\lg P_{CO_2}$	$\lg[CO_3^{2-}]$	$\lg[HCO_3^-]$	$\lg[NH_4^+]$	$\lg[NH_3]$	I	$\lg[CO_2]$	$\lg[OH^-]$	$\lg k'_1$	$\lg k'_{1,2}$	$\lg k'_{p1}$	$\lg K'_1$	$\lg a_{CO_3^{2-}}$	$\lg a_{OH^-}$
0.1	-2.61	-1.81	-1.07	-0.94	-1.07	0.13	-4.08	-4.66	-3.92	-7.66	-6.19	-4.52	-2.29	-4.77
0.15	-2.46	-1.59	-0.91	-0.76	-0.91	0.20	-3.93	-4.64	-3.96	-7.67	-6.20	-4.49	-2.14	-4.76
0.2	-2.36	-1.43	-0.79	-0.62	-0.79	0.27	-3.83	-4.64	-4.00	-7.68	-6.21	-4.47	-2.03	-4.76
0.25	-2.28	-1.31	-0.70	-0.52	-0.70	0.35	-3.75	-4.63	-4.02	-7.69	-6.21	-4.46	-1.95	-4.76
0.3	-2.21	-1.21	-0.62	-0.44	-0.62	0.42	-3.69	-4.63	-4.05	-7.69	-6.22	-4.45	-1.88	-4.76
0.45	-2.07	-0.99	-0.46	-0.26	-0.46	0.66	-3.55	-4.63	-4.11	-7.72	-6.24	-4.43	-1.74	-4.76
0.5	-2.03	-0.93	-0.42	-0.21	-0.42	0.74	-3.51	-4.63	-4.12	-7.72	-6.25	-4.43	-1.70	-4.76
0.6	-1.97	-0.83	-0.35	-0.13	-0.34	0.90	-3.45	-4.64	-4.16	-7.74	-6.26	-4.42	-1.64	-4.76
0.75	-1.89	-0.71	-0.26	-0.02	-0.26	1.14	-3.37	-4.65	-4.20	-7.76	-6.29	-4.42	-1.56	-4.77
1	-1.79	-0.55	-0.14	0.11	-0.14	1.56	-3.27	-4.68	-4.26	-7.81	-6.32	-4.43	-1.46	-4.77
1.25	-1.71	-0.44	-0.05	0.21	-0.05	1.98	-3.20	-4.70	-4.32	-7.85	-6.36	-4.44	-1.38	-4.77
1.5	-1.65	-0.34	0.02	0.29	0.02	2.42	-3.14	-4.74	-4.38	-7.89	-6.40	-4.46	-1.32	-4.77
1.8	-1.59	-0.24	0.09	0.38	0.09	2.94	-3.08	-4.78	-4.44	-7.95	-6.45	-4.49	-1.26	-4.78
2	-1.56	-0.19	0.13	0.42	0.13	3.30	-3.05	-4.80	-4.49	-7.98	-6.49	-4.51	-1.22	-4.78
2.2	-1.52	-0.14	0.17	0.47	0.17	3.66	-3.02	-4.83	-4.53	-8.02	-6.52	-4.53	-1.19	-4.78
2.2	-3.50	-0.50	-0.97	-0.13	0.56	1.05	-5.00	-3.73	-4.20	-7.76	-6.27	-4.43	-1.32	-3.84
2	-3.50	-0.54	-0.98	-0.17	0.52	0.97	-4.99	-3.74	-4.18	-7.75	-6.26	-4.43	-1.35	-3.85
1.8	-3.50	-0.58	-1.00	-0.20	0.47	0.89	-4.99	-3.75	-4.16	-7.74	-6.25	-4.43	-1.38	-3.87
1.5	-3.50	-0.66	-1.02	-0.27	0.39	0.76	-4.99	-3.77	-4.13	-7.73	-6.24	-4.43	-1.42	-3.89
1.25	-3.50	-0.73	-1.05	-0.34	0.31	0.65	-4.98	-3.79	-4.11	-7.72	-6.23	-4.43	-1.47	-3.91
1	-3.50	-0.82	-1.09	-0.42	0.21	0.53	-4.98	-3.81	-4.08	-7.71	-6.22	-4.44	-1.53	-3.94
0.75	-3.50	-0.94	-1.14	-0.52	0.08	0.42	-4.98	-3.85	-4.05	-7.69	-6.21	-4.45	-1.61	-3.98
0.6	-3.50	-1.04	-1.17	-0.60	-0.02	0.34	-4.98	-3.88	-4.02	-7.69	-6.21	-4.46	-1.67	-4.01
0.5	-3.50	-1.11	-1.21	-0.66	-0.11	0.29	-4.98	-3.91	-4.00	-7.68	-6.20	-4.47	-1.72	-4.04
0.45	-3.50	-1.16	-1.22	-0.70	-0.15	0.27	-4.98	-3.93	-3.99	-7.68	-6.20	-4.47	-1.75	-4.05
0.3	-3.50	-1.33	-1.30	-0.84	-0.34	0.19	-4.97	-3.99	-3.96	-7.67	-6.20	-4.50	-1.87	-4.11
0.25	-3.50	-1.41	-1.33	-0.91	-0.42	0.16	-4.97	-4.02	-3.94	-7.67	-6.19	-4.51	-1.93	-4.14
0.2	-3.50	-1.51	-1.37	-0.98	-0.53	0.13	-4.97	-4.06	-3.92	-7.66	-6.19	-4.52	-2.00	-4.17
0.15	-3.50	-1.64	-1.43	-1.08	-0.66	0.11	-4.97	-4.12	-3.90	-7.66	-6.19	-4.54	-2.09	-4.22
0.1	-3.50	-1.83	-1.51	-1.22	-0.86	0.08	-4.97	-4.20	-3.88	-7.66	-6.19	-4.56	-2.23	-4.29

suspension in the Moskvin's Np saturated solution. We then do not think, as suggested by Rai and Ryan [85RAI/RYA], that some Np(VI) can also be seen in this spectrum. SPECTRA SHOULD BE CHECKED AGAIN, WHEN DISCUSSING [95DEL] IN THIS APPENDIX.

2.1.3.Solubility: solid phase

Np(IV) was introduced as $Np(OH)_4.xH_2O$, that was prepared as in [71MOS3]. Moskvin implicitly supposed, that this solid still controls the solubility during his measurements; but he did not report any characterisation of his solid phase after equilibration. Two years later he will publish [73KHA/MOS] infrared spectra of $K_6Np(CO_3)_5.xH_2O$, that was prepared as Pu(IV) similar compounds $M_6Pu(CO_3)_5.xH_2O$ and $M_4Pu(CO_3)_4.xH_2O$ where M can be Na, K or NH_4 [58GEL/ZAI1] [58GEL/ZAI2] [59GEL/ZAI]. These types of compounds are precipitated out from concentrated M_2CO_3 aqueous-ethanol solutions. Moskvin did certainly not ignore these Gel'man's old works, since he published with him earlier on similar subjects. Anyhow, for this reason Moskvin's interpretation of its solid phase and then (again) of his soluble complex is not reliable. Still, Moskvin certainly prepared Np(IV) soluble species in concentrated ammonium carbonate solutions.

The preparation conditions of the solid are similar to the one used in previous soviet works to prepare solid M-actinide(IV) carbonate ($M^+ = Na^+$, K^+ or NH_4^+). This method avoids the possible non-reversible formation of polymeric actinide(IV) in near neutral aqueous solutions, this possibly occurred in a later work [78SAI/UEN]. His solubility results are not much different from the Ce(IV) or Th(IV) solubility in similar conditions [73DER/FAU3], that is controlled by $Na_6An(CO_3)_5.12H_2O$, and is due to at least one soluble carbonate complex.



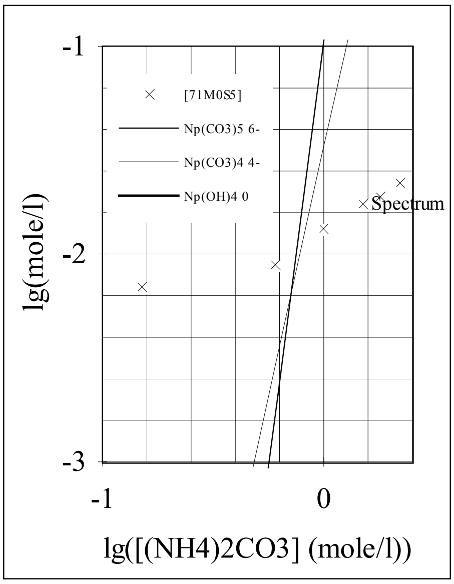


Figure [71MOS5]-1 pH measured by Moskvin [71MOS5] during its solubility measurement of Np(IV, V and VI) in $(NH_4)_2CO_3$ solutions and calculated in this review using the data of the tables [71MOS5]-1. We assume, that there was either no exchange of carbonic gas with the air (solid line) or (dashed line) equilibrium with the air only for carbonic gas (not for ammoniac gas).

Figure [71MOS5]-4 Np(IV) solubility measured by Moskvin in $(NH_4)_2CO_3$ solutions. lg is $\log_{10}$. The spectrum of the supernatant solution, where $\lg[(NH_4)_2CO_3] = 0.18$ (indicated on the figure), is also shown in the same publication [71MOS5]. It has also been observed later [77SAI/UEN], [81WES/SUL] [93LI/KAT] and [95DEL] : it is the spectrum of the Np(IV) carbonate limiting complex. It is consistent with the solubility calculation shown on the figure. For this calculation we assume, as in the figure [71MOS5]-3, that this limiting complex is $Np(CO_3)_5^{6-}$. It would be dissociated into $Np(CO_3)_4^{4-}$, and $Np(OH)_4^0$ concentration is negligible (less than 10^{-8} M). The calculations also indicate, that the solubility is not controlled by $Np(OH)_{4(s)}$ solid phase. $(NH_4)_6Np(CO_3)_5.12H_2O$ and other solid phases (see text), where certainly slowly precipitating.

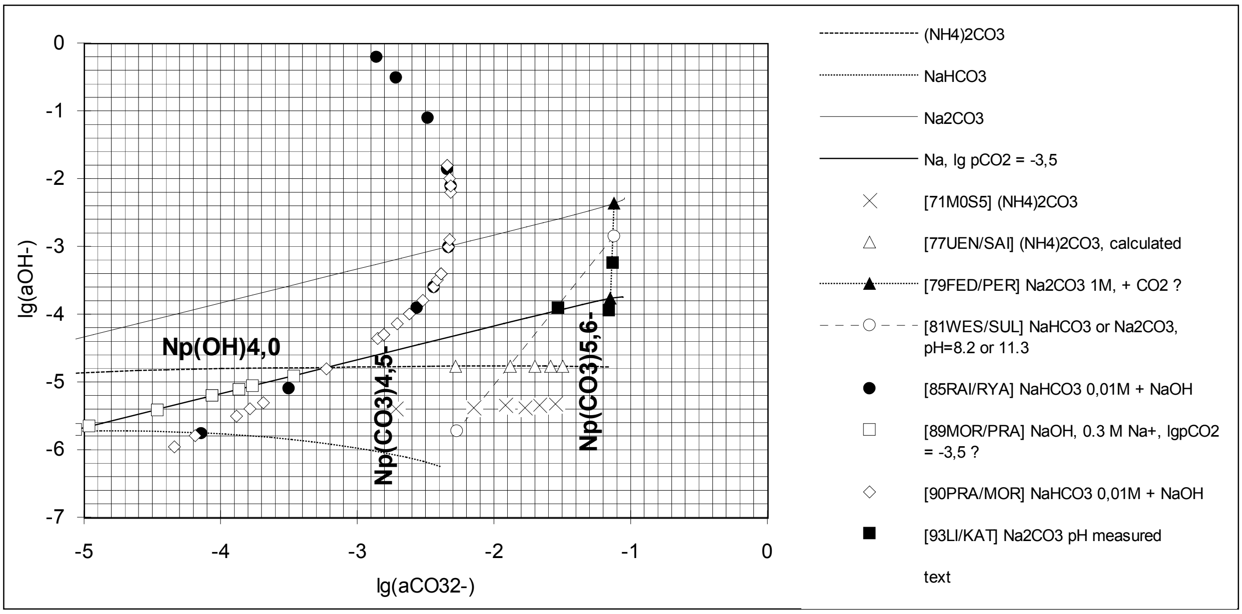


Figure [71MOS5]-2 Comparison of the carbonate speciation used in the published works on Np(IV) solubility and solution chemistry in carbonate media. lg is $\log_{10}$. Only the works of [85RAI/RYAN], [89MOR/PRA] and [90PRA/MOR] were performed in similar chemical conditions, and can then be easily compared. If only $Np(OH)_4$, $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ soluble complexes are formed, a predominance diagram is suggested (by the places, where the names of these species are written). If the limiting complex is $Np(CO_3)_5^{6-}$, it is stabilised at high ionic strength, this reason, can explain, that it is obtained in concentrated carbonate or bicarbonate media (figure [71MOS5]-4).

2.1.4.Solubility: soluble complexes

Moskvin has assumed, that the solubility of Np(IV) is due to $Np(OH)_4CO_3^{2-}$, and then proposed its formation constant, $\log_{10}\beta_{4,1} = 53.045 \pm 0.015$. From a later work [85RAI/RYA], this review calculates (see the discussion on [85RA/RYA] in this appendix), that this formation constant is certainly less than 47. In a similar work on plutonium, where they give more details on their calculations, Moskvin and Gel'man had proposed earlier [58MOS/GEL] the formation of $Pu(OH)_4CO_3^{2-}$ with a similar value for the formation constant. In both cases the interpretation is incorrect (see the present discussion and the one about [58MOS/GEL] in this appendix. It is clear in this previous [58MOS/GEL] Pu work, that the authors knew, that they could not decide

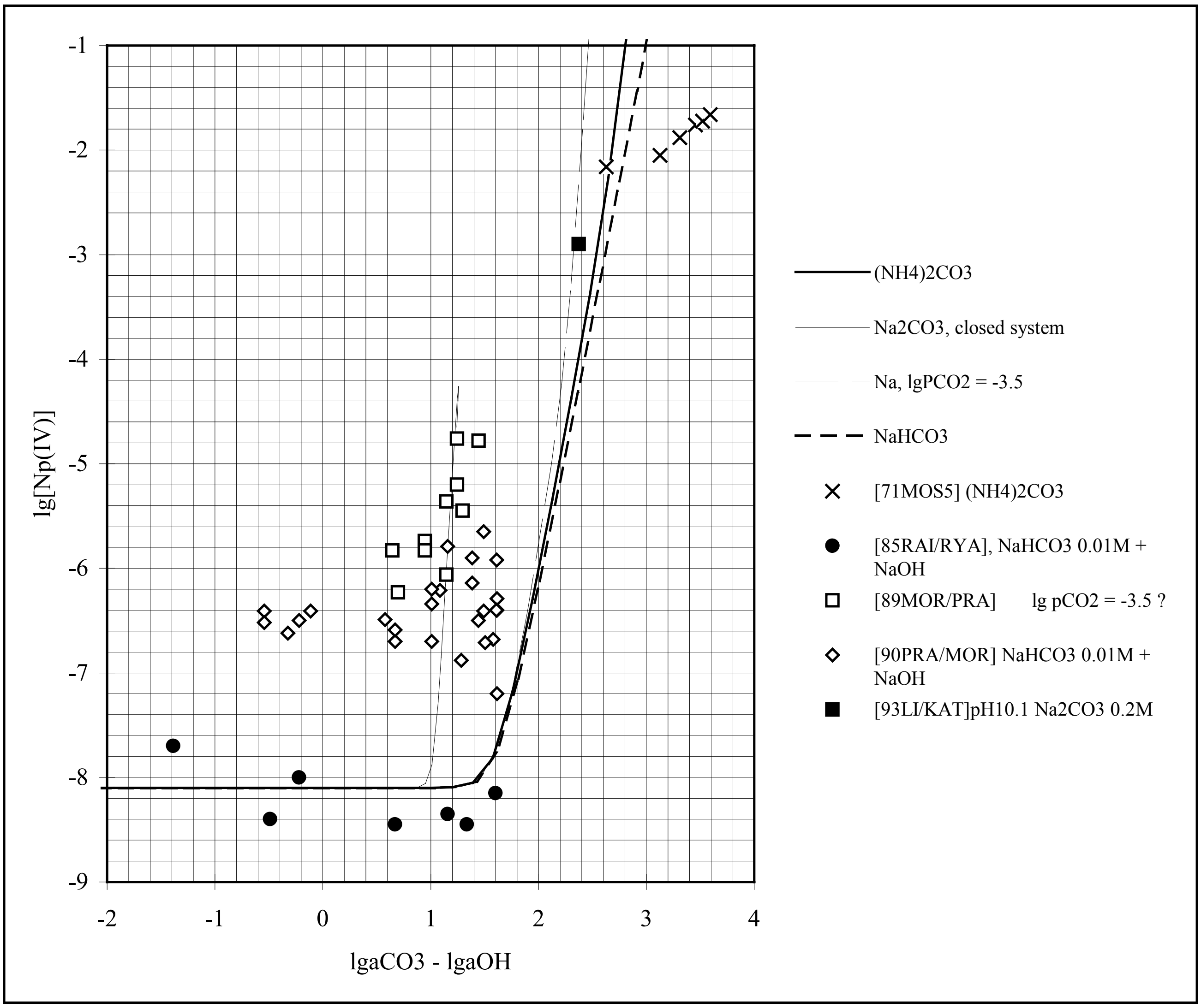
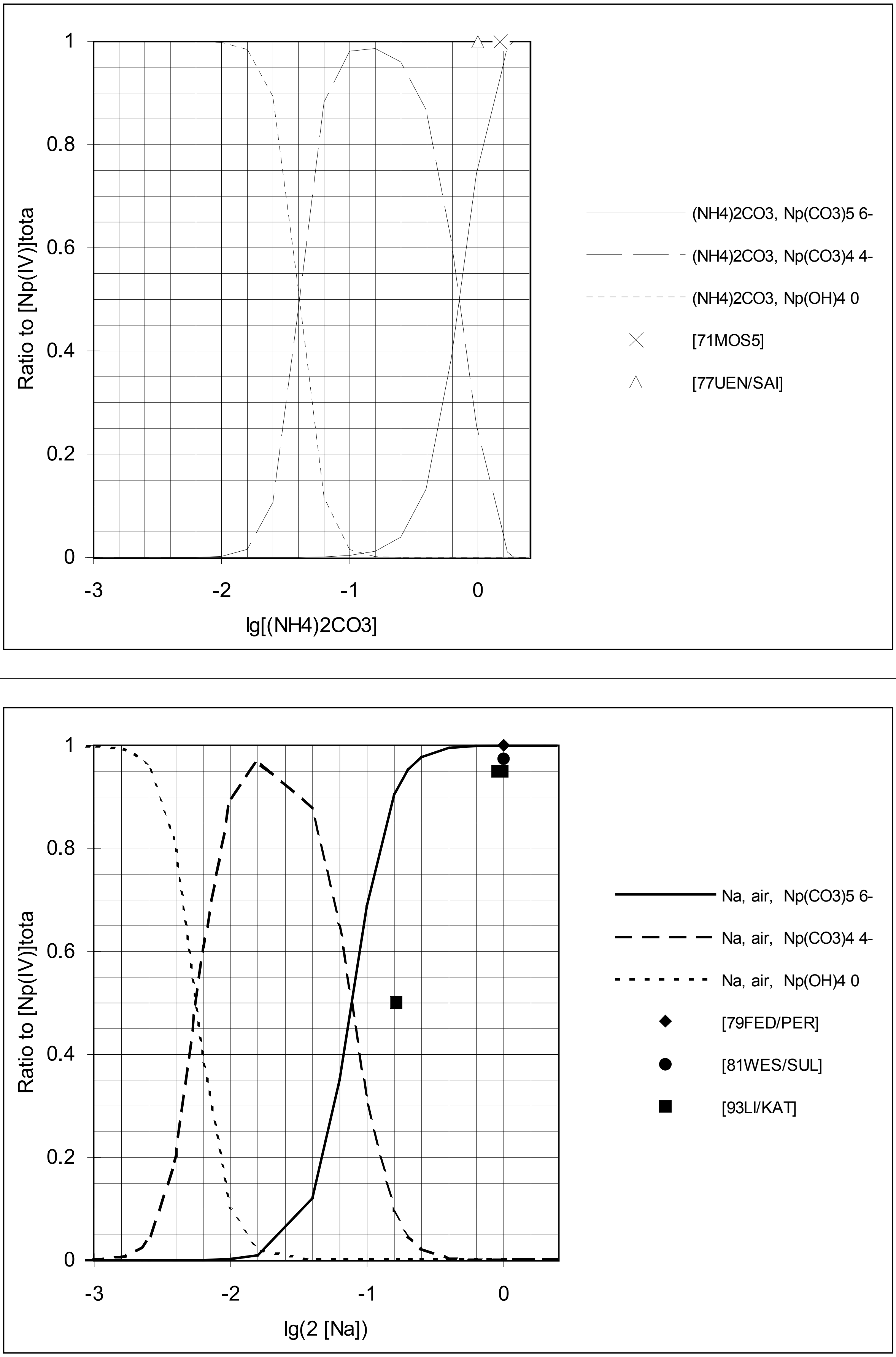


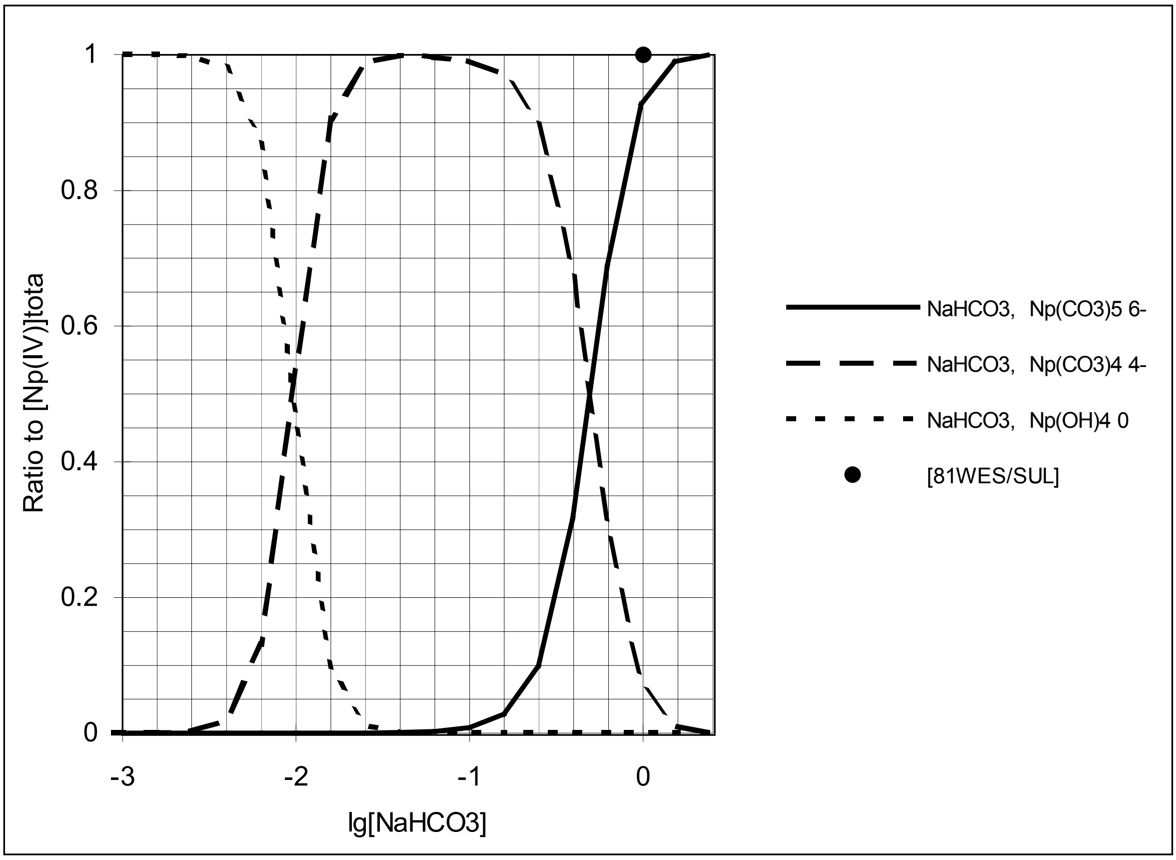
Figure [71MOS5]-3 Np(IV) solubility in carbonate media. lg is $\log_{10}$. The aim of this figure is not really to support the selection of some thermodynamic data, it is rather to point out, that all the published solubility works are consistent with the formation of $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ complexes, whose stability's are similar to the U and Pu ones. Numerical values for the calculated solubility (line) are in table [79FED/PER]-1c. THEY ARE STILL TO BE DISCUSSED WITHIN THE REVIEW, AND [95DEL] SHOULD PRODUCE MORE RELIABLE NUMERICAL VALUES. It is drawn for $Np(OH)_{4s}$. $M_6Np(CO_3)_5.12H_2O$ (here M = Na or NH_4) and other solid phases (see text) certainly limit the Np(IV) solubility in concentrated M_2CO_3 solutions, some of these solids might be poorly crystallised, the [93LI/KAT] point and some of the [71MOS5] ones might be oversaturated with these phases. The differences between the calculated curves are mostly due to the activity coefficients, mainly to the $Np(CO_3)_5^{6-}$ one. See other explanations on the figure [90PRA/MOR]-1

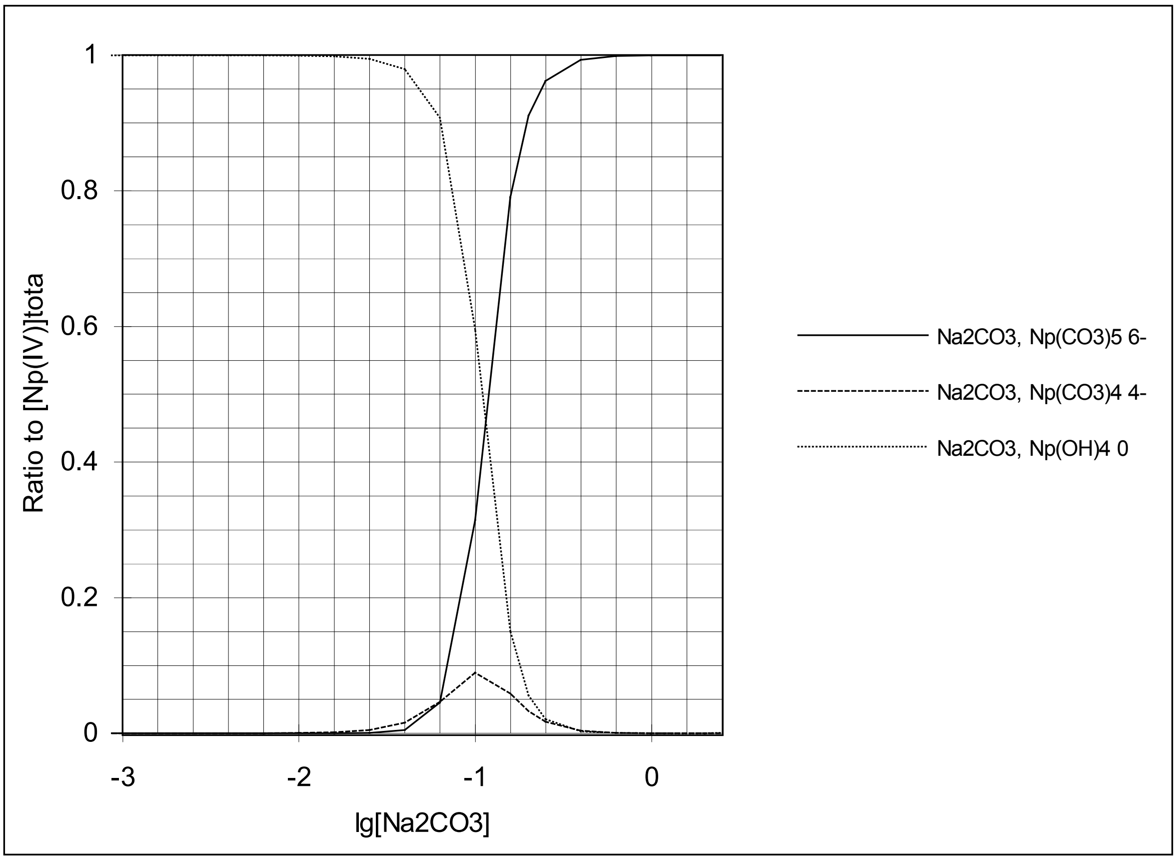
the exact stoichiometry of their soluble complex). The numerical values are similar only because the methodology is the same, and because Np(IV) and Pu(IV) are chemical analogues. Rai and Ryan [85RAI/RYA] give "a variety of reasons for completely rejecting such carbonate formation constant values".

They explain, that chemical reactivity can be used to predict a lower value. This mainly concerns (Pu or Np)CO_3^{2+} and not $Np(OH)_4CO_3^{2-}$. They have calculated, using Moskvin's formation constant, a very high solubility of Pu(IV) in conditions, where it is known to be highly insoluble. Rai and Ryan also pointed out that: "the method used [by Moskvin] to calculate [the $Np(OH)_4CO_3^{2-}$ formation constant] was completely erroneous. [... because he makes the] assumption, that total carbonate plus bicarbonate is entirely carbonate at pH values, where bicarbonate predominates and the carbonate to bicarbonate ratio is pH dependent, and provision of no evidence, that the assumed "$Np(OH)_4xH_2O$" was the equilibrium solid phase in these Np(IV)-saturated concentrated ammonium carbonate solutions, whereas [other actinide(IV) solid phases] have been isolated from ammonium carbonate solutions."

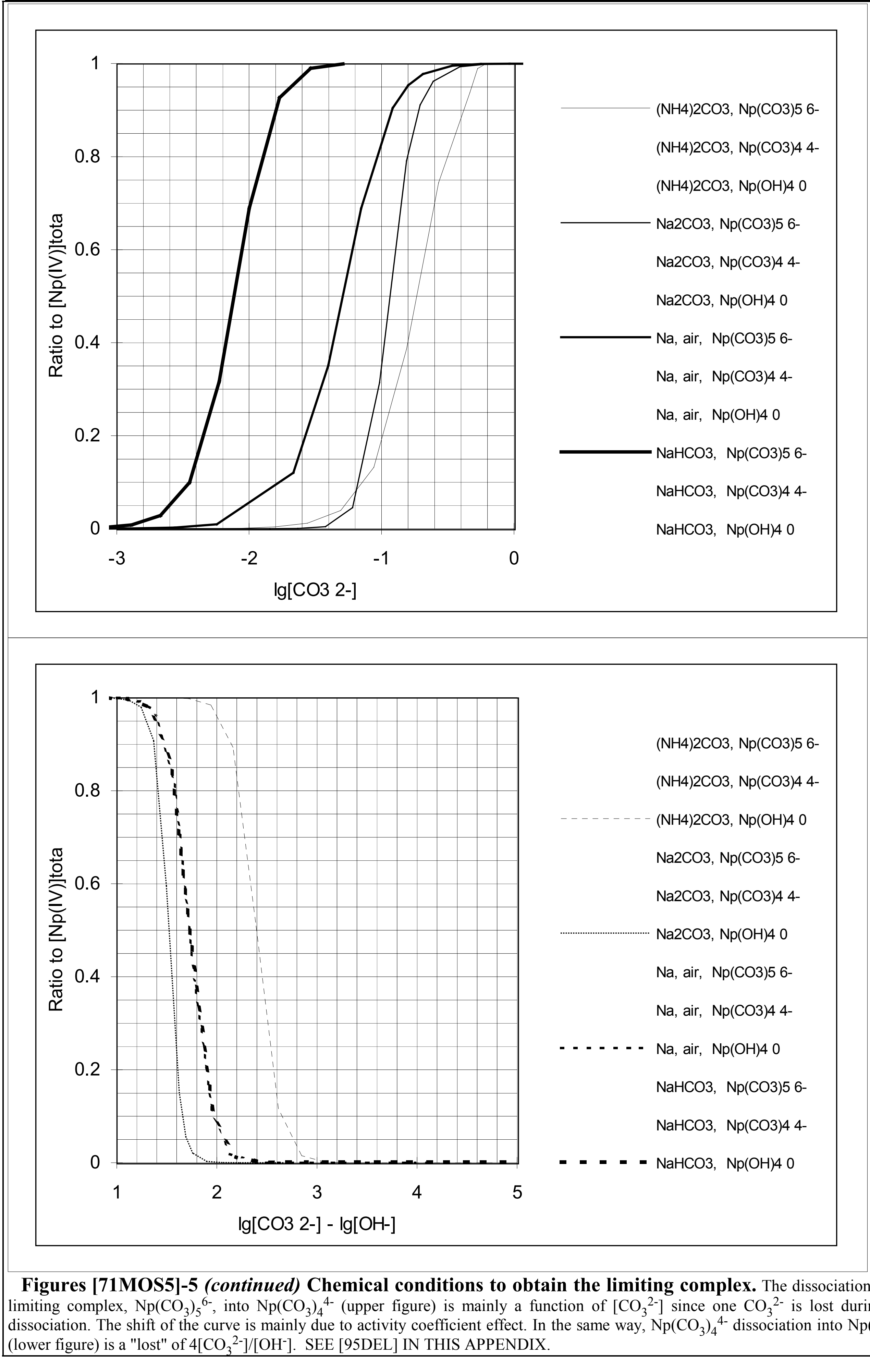


Figures [71MOS5]-5 Chemical conditions to obtain the limiting complex. Its spectrum has been observed in M_2CO_3, where (M = Na or NH_4) [71MOS5][77SAI/UEN][81WES/SUL][93LI/KAT], and $NaHCO_3$ solutions [81WES/SUL]. Our speciation calculation, are consistent with the published spectra, and [79FED/PER] electrochemical measurements then also involved the limiting complex. This interpretation has just been recently confirmed qualitatively [95DEL]: IT SHOULD BE CHECKED QUANTITATIVELY IN A FURTHER VERSION OF THIS REVIEW. Speciation, calculated as in figure [71MOS5]-3 and 4, is plotted as a function of the $\log_{10}$ of total carbonate concentration (mol./l). In the bottom figure, a Na_2CO_3 solution is supposed to be equilibrated with the air ($P_{CO_2}=10^{-3.5}$atm; but it was more than this value in [93LI/KAT]). SEE [95DEL] IN THIS APPENDIX.

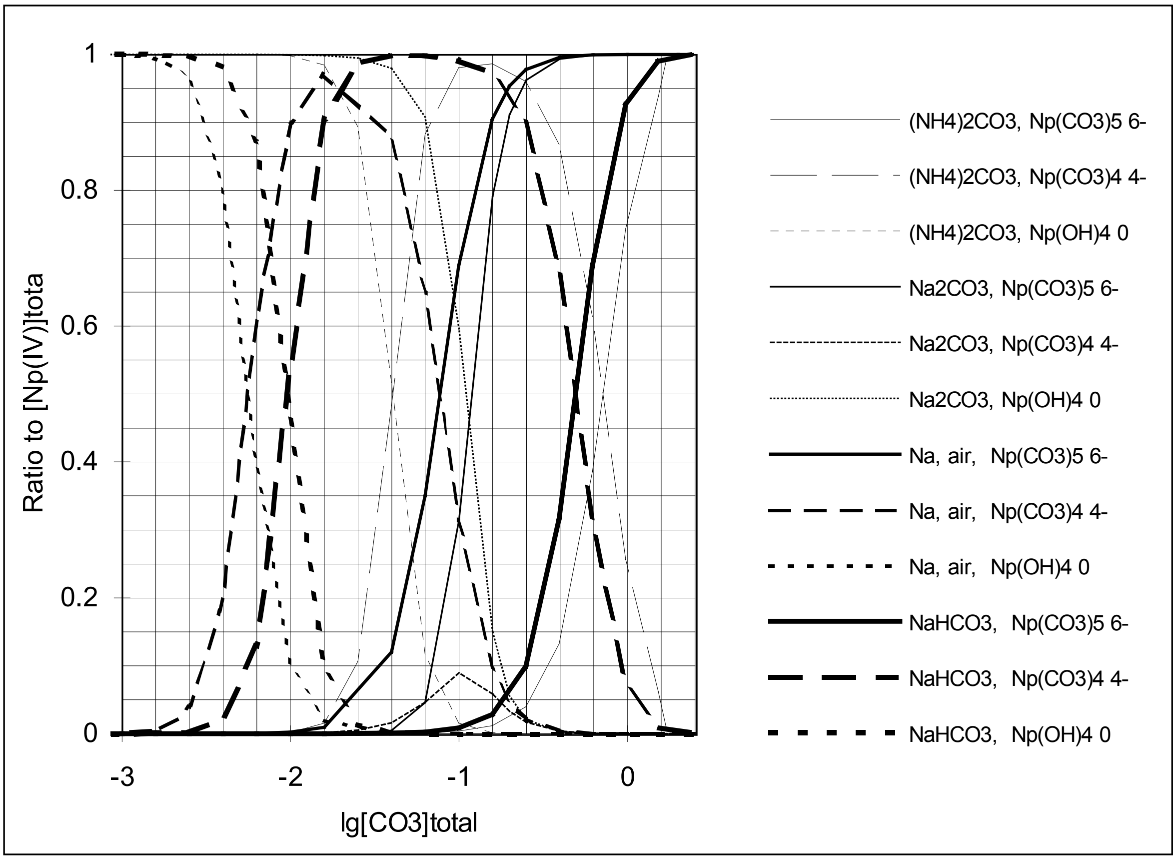




Figures [71MOS5]-5 ***(continued)*** **Chemical conditions to obtain the limiting complex.** In 1 M $NaHCO_3$ solution, the limiting complex is the major species, and this calculation is consistent with Wester and Sullivan observation [81WES/SUL]. In Na_2CO_3 solutions, P_{CO_2} is very low, so it has probably never been the experimental conditions of most of the published works (see text): in these conditions, when [Na_2CO_3] is decreased, the limiting complex should be dissociated into hydroxide and not pure carbonate complex. Solubility would then be too low to observe any spectral change. SEE [95DEL] IN THIS APPENDIX.



Figures [71MOS5]-5 *(continued)* Chemical conditions to obtain the limiting complex. The dissociation of the limiting complex, $Np(CO_3)_5^{6-}$, into $Np(CO_3)_4^{4-}$ (upper figure) is mainly a function of $[CO_3^{2-}]$ since one CO_3^{2-} is lost during this dissociation. The shift of the curve is mainly due to activity coefficient effect. In the same way, $Np(CO_3)_4^{4-}$ dissociation into $Np(OH)_4^0$ (lower figure) is a "lost" of $4[CO_3^{2-}]/[OH^-]$. SEE [95DEL] IN THIS APPENDIX.



Figures [71MOS5]-5 ***(continued)*** **Chemical conditions to obtain the limiting complex.**

We are making similar comments above: this review agrees with Rai and Ryan's analysis [85RAI/RYA] of Moskvin's interpretations except for minor points, typically they say "β_2, [...] β_3 [...] β_4 [...] should be smaller than β_1", this does not seem to be correct because the comparison of the numerical values of these constants cannot be so straightforward (they have not the same units).

Np solubility in carbonate media is a four component system: redox potential, solubility (or total Np concentration) and two extra parameters for the carbonate speciation (typically pH and [CO_3^{2-}]). It is then not straightforward to compare different solubility works in various carbonate media. Still it is clear, that no other published work was performed in exactly the same carbonate medium (figure [71MOS5]-2). It is also well known for a long time (see the beginning of the discussion of [71MOS5] in this appendix), that the actinides(IV) are soluble in concentrated carbonate solutions, where their solubility can be controlled by some $M_{2n-4}An(CO_3)_n.xH_2O$ solid phases. There is then no evidence of any contradiction between Moskvin's data and other published work (Figures [71MOS5]-3, 4 and the § just below): only Moskvin's interpretation is "unbelievable", rely on "completely erroneous assumptions" and is certainly "completely incorrect" as first clearly pointed out in [85RAI/RYA].

When it is controlled by $Np(OH)_4$ solid and $Np(OH)_4^0$ soluble complex Np(IV) solubility is very low: less than 10^{-8} M (this value is higher than the U and Pu ones, but it is probably the good one and not only the ^{237}Np detection limit, see [85RAI/RYA] and § VI.3.2.4. of this review). This is even the case in 0.01 M CO_3^{2-} solutions [85RAI/RYA]: the difference in $\log_{10}a_{CO_3^{2-}}$ with some Moskvin's solutions is no more than 1 unit $\log_{10}$ (Figure [71MOS5]-2). Moskvin measured a solubility five orders of magnitude higher than Rai and Ryan one. The solubility increases then with a slope of about five, the soluble carbonate complex should then contain at least five carbonate ; but, depending on the experimental procedures (Moskvin gives only a few details on them), some of the points in the less concentrated ammonium carbonate solutions might well be oversaturated. This is illustrated in figure [71MOS5]-3, where we are using for the formation constants of the $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ complexes, the values of table [79FED/PER]-1c. The aim of this figure is not really to support the selection of some thermodynamic data, it is rather to point out, that all the published solubility works are consistent with the formation of $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ complexes, whose stability's are similar to the U [92GRE/FUG] and Pu [92CAP] ones. $An(CO_3)_4^{4-}$ and $An(CO_3)_5^{6-}$ certainly exist for An = Np in some conditions: they have been proposed for Ce(IV), Th(IV) [73DER/FAU], U(IV) [92GRE/FUG] and Pu(IV) [92CAP].

2.2. [76FRO/CHI1]

Frolova, L.M., Chistyakov, V.M., Ermakov, V.A., Rykov, A.G. *Kinetics and mechanism of the oxidation of neptunium(IV) by persulfate ions in carbonate solutions*, Radiokhimiya, 18 (2) (1976) 276-280 Engl. transl.: Sov. Radiochem., 18 (2) (1976) 249-253.

The apparent rate constant, k, of the reaction Np(IV) + Np(VI) → 2 Np(V) decreases, when the K_2CO_3 concentration of the solution is increased from 1.71 to 4.00 M. This confirms the results of [76FRO/CHI2]. The slope of $\log_{10}$k versus $\log_{10}[K_2CO_3]$ seems to be nearly -2. We do not find a straightforward interpretation for this. According to the present review, the global reaction in these conditions could be

$$Np(CO_3)_5^{6-} + NpO_2(CO_3)_3^{4-} \rightarrow 2\ NpO_2(CO_3)_3^{5-} + 2\ CO_2.$$

The equilibrium P_{CO_2} in this medium is practically constant; but it is not buffered. It could then increase during (or before) the experiment (through equilibration with the air) inducing a decrease of pH. At equilibrium, the pH would increase with $[K_2CO_3]$. The authors did not measure the pH. They should have then observed a decrease of k with the increase of pH. The limiting kinetic reaction is then probably not the same in acidic and carbonate media as pointed out by the authors. No information about the stoichiometry of the species, and no thermodynamic data can be deduce from this work.

2.3. [76FRO/CHI2]

Frolova, L.M., Chistyakov, V.M., Ermakov, V.A., Rykov, A.G. *Kinetics of the reaction of neptunium(IV) with neptunium(VI) in potassium carbonate solutions*, Radiokhimiya, 18 (2) (1976) 281-283 Engl. transl.: Sov. Radiochem., 18 (2) (1976) 254-256.

See [76FRO/CHI1].

2.4. [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.

The Np(IV) carbonate solution and solid are prepared by adding a Np^{4+} acidic solution in carbonate solutions. The authors seem to have used quite a poor experimental procedure: they say, that they had to centrifuge some undissolved hydroxide. This is consistent with actinide(IV) chemistry (see the beginning of the discussion of [71MOS5] in this appendix) and we expect, as for plutonium [83KIM/LIE], that possible formation of unwanted fresh soluble polymeric hydroxide is dissociated in the concentrated carbonate working solutions. This is confirmed by the absorption spectrum of the resulting 7.04 mM Np(IV) solution in 1 M $(NH_4)_2CO_3$: it is the spectrum of (MAINLY: SEE [95DEL] IN THIS APPENDIX] the known [71MOS5] Np(IV) carbonate limiting complex, that has also been confirmed later in other concentrated carbonate media (Figure [71MOS5]-2).

Addition of the big heaxammine cobalt(III) cation lowers the solubility (comparison with [71MOS5]) as expected (see the possible effect of big cations on Np(IV) solubility in the discussion of [71MOS5] in this appendix). The composition of the solid is proposed from chemical analysis (and analogy with Th and Pu in [70UEN/HOS]): $[Co(NH_3)_6]_2[Np(CO_3)_5].4H_2O$. Its solubility increases with the concentration of $Co(NH_3)_6Cl_3$, and also with the concentration of $(NH_4)_2CO_3$ except for the last point in 0.9 M $(NH_4)_2CO_3$. This behaviour could be attributed to the formation of soluble complex with unknown stoichiometry, maybe containing the hexaamine cobalt cation, or could be attributed to strong ionic strength effect, possibly ion pairing of the highly negative Np(IV) carbonate limiting complex with the ammonium cation or/and with again the hexaamine cobalt cation: not a unique qualitative interpretation can be proposed. No thermodynamic data can then be derived from this work.

Table [77SAI/UEN]-1, [79FED/PER]-1, [84VAR/HOB]-1 Speciation in carbonate solutions, calculated with the parameters of the tables [71MOS5]-1a and b. M is the initial concentration of $(NH_4)_2CO_3$. lg is $\log_{10}$. The definitions of the constants are in table [71MOS5]-1b (name); but they are here in molar (and not molal) units. Speciation is used in this appendix to draw the figures and to perform the calculations. lg is $\log_{10}$.

M	$\lg P_{CO_2}$	$\lg[CO_3^{2-}]$	$\lg[HCO_3^-]$	$\lg[NH_4^+]$	$\lg[NH_3]$	I	$\lg[CO_2]$	$\lg[OH^-]$	lg k'$_1$	lg k'$_{1,2}$	lg k'$_{p1}$	lg K'$_1$	lg $a_{CO_3^{2-}}$	lg a_{OH^-}
$(NH_4)_2CO_3$ closed system.														
0.10	-2.60	-1.79	-1.06	-0.92	-1.06	0.14	-4.07	-4.66	-3.93	-7.66	-6.19	-4.52	-2.28	-4.77
0.31	-2.21	-1.20	-0.62	-0.43	-0.62	0.43	-3.68	-4.63	-4.05	-7.69	-6.22	-4.45	-1.88	-4.76
0.50	-2.03	-0.92	-0.42	-0.21	-0.41	0.74	-3.51	-4.63	-4.13	-7.73	-6.25	-4.43	-1.70	-4.76
0.70	-1.91	-0.74	-0.28	-0.05	-0.28	1.06	-3.39	-4.65	-4.19	-7.76	-6.28	-4.42	-1.58	-4.77
0.90	-1.83	-0.61	-0.19	0.06	-0.18	1.38	-3.31	-4.67	-4.24	-7.79	-6.31	-4.42	-1.50	-4.77
Na_2CO_3 closed system, or ($\lg P_{CO_2}$=-3.50) the carbonic gas is equilibrated with the air.														
				$\lg[Na^+]$										
1.00	-6.28	0.00	-2.23	0.30		2.99	-7.75	-2.23	-4.45	-7.75	-6.28		-1.12	-2.37
1.00	-3.50	-0.03	-0.85	0.30		2.93	-4.98	-3.63	-4.45	-7.75	-6.28		-1.15	-3.77
2.00	-6.37	0.30	-2.24	0.60		5.99	-7.85	-2.24	-4.79	-7.85	-6.37		-1.05	-2.30
2.00	-3.50	0.28	-0.82	0.60		5.92	-4.98	-3.69	-4.79	-7.86	-6.38		-1.06	-3.74
K_2CO_3 closed system, or ($\lg P_{CO_2}$=-3.50) the carbonic gas is equilibrated with the air.														
				$\lg[K^+]$										
1.00	-6.41	0.00	-2.20	0.30		2.99	-7.89	-2.20	-4.40	-7.89	-6.41		-1.01	-2.25
1.00	-3.50	-0.04	-0.77	0.30		2.91	-4.99	-3.68	-4.40	-7.89	-6.41		-1.05	-3.72

Table [81WES/SUL]-1 Speciation in Na_2CO_3 (first line) **and $NaHCO_3$** (second line) **solutions**

				$\lg[Na^+]$								pH		
1.00	-3.58	0.00	-1.75	0.30		2.99	-5.05	-2.70	-4.45	-7.75	-6.28	11.2	-1.12	-2.84
1.00	-0.66	-1.39	-0.04	0.00		1.04	-2.14	-5.58	-4.23	-7.71	-6.23	8.3	-2.27	-5.73

2.5. [79FED/PER]

Fedoseev A. M., Peretrukhin V. F., Krot N. N. *Redox potentials of couples of ions of transuranium elements in carbonate solutions*. Doklady Akademii Nauk SSSR 244 (5) (1979) 1187-1190. Engl. trans.: Doklady Phys. Chem. 244 (1979) 139-141.

The formal potential of the Np(V)/Np(IV) and Np(IV/III) redox couples are measured respectively by potentiometry probably at a mercury electrode, and in 1 M K_2CO_3 solution by polarography. There is no much experimental detail. The Np(IV) carbonate solution is prepared by adding solid oxalate into it. As expected the attainment of the Np(V)/Np(IV) equilibrium is slow: the authors waited 7 hours. This might not be enough for this type of equilibrium and for this methodology. It was difficult to obtain a stable indication of the electrode. "... only an extremely approximate value close to 0.1 V" is finally proposed. This value has been confirmed later [84VAR/HOB] with no better precision for the same reason. No reliable thermodynamic data can then be calculated from it.

2.5.1.pH, P_{CO_2} and speciation

The carbonic gas partial pressure is a critical parameter (see below), when the potential of the solution is controlled by the Np(V)/Np(IV) couple. Using the constants selected in this review, we calculate the speciation in 1 M Na_2CO_3 and K_2CO_3 solutions in closed (no exchange with the air) and in open (equilibration with the air) systems (Table [79FED/PER]-1). As for the review on [71MOS5] in this appendix, we are using concentration of anions, but activity of reactive cations (Table [79FED/PER]-1).

The authors probably stirred the solution to attain equilibrium: this usually induces mixing with the gas above the solution within a few minutes; but as soon as P_{CO_2} has reached its equilibrium value, it is no more possible to lower it back with the same procedure (simply stirring the solution with a pure inert gas above it). The author said, that they had to avoid traces of oxygen to stabilise their potential measurement. The solution was then (at least at the end) protected from the air; but probably not along all the procedure.

Table [79FED/PER]-2 [84VAR/HOB]-1 Tentative reinterpretation of redox measurements. The redox potentials of the Np(V)/Np(IV) and of the Np(IV)/Np(III) couple were measured by [79FED/PER] in 1 M Na_2CO_3 and in 1 M K_2CO_3 solution respectively: when nothing else is stated the results of the reinterpretation of these measurements are here tabulated. The speciation of the table [79FED/PER]-1 is used, assuming equilibrium with the carbonic gas of the air. The redox potential of the Np(IV)/Np(III) couple measured by [84VAR/HOB] in 2 M Na_2CO_3 and 1 M K_2CO_3, are reinterpreted in the same way. The same ε values are usually taken in both media, in K_2CO_3 medium the uncertainties are increased. Their unit is kg/mol. The $\log_{10}$ values of the equilibrium constants are tabulated. lg is $\log_{10}$. $\beta'_{5IV} = [An(CO_3)_5^{6-}]/\ a_{An^{4+}}\ /[CO_3^{2-}]^5$, the molal activity of the aquo ion, but the molarity of the other species are used in this equilibrium constant. $\beta°_{5IV}$ is the classical standard formation constant of the limiting complex of An(IV), it is β'_{5IV} at zero ionic strength. In the same way $\beta'_{3V} = [AnO_2(CO_3)_3^{5-}]/\ a_{AnO_2^+}\ /[CO_3^{2-}]^3$ and $\beta'_{3III} = [An(CO_3)_3^{3-}]/\ a_{An^{3+}}\ /[CO_3^{2-}]^3$. Their values are taken from the references written as foot notes or calculated from them. When they do not refer to any foot note we calculate them (see text). In the second Np column ("Np from E(IV/III)"), the values are deduced from redox measurements of the Np(IV)/Np(III). In the first Np column ("Np"), all the other values are tabulated, many of them are deduced from redox measurements of the Np(V)/Np(IV) redox couple. The aim of this table is only to present the results of our calculations, not to propose new equilibrium constants. For this, see the discussion.

	U	Np	Np from E(IV/III)	Pu	Am
$\varepsilon(An(CO_3)_3^{3-}, Na^+)$					$-0.11^a \pm 0.25$
$\varepsilon(An(CO_3)_5^{6-}, Na^+)$	$-0.07^b \pm 0.15$	0.45 ± 0.70		$0.96^b \pm 0.10$	
$\varepsilon(AnO_2(CO_3)_3^{5-}, Na^+)$		$-0.36^d \pm 0.08$			
$\lg\beta°_{3III}$		$5.6^i \pm 1.8$		$^e\pm$	$14.0^a \pm 1.5$
$\lg\beta°_{5IV}$	$34.0^b \pm 0.9$	39.2 ± 3.7	36.5 ± 3.1	$32.2^c \pm 2.0$	$37^g \pm 2$
from [84VAR/HOB]1M K_2CO_3			36.1 ± 3.1		
from [84VAR/HOB]2M Na_2CO_3			35.2 ± 3.8		
$\lg\beta'_{5IV}$ in1 M Na_2CO_3	$37.4^b \pm 1.0$	41.5 ± 3.4		$33.5^c \pm 2.0$	
in 1 M K_2CO_3	$38.4^b \pm 1.3$		39.7 ± 1.7	$34.4^c \pm 2.2$	
[84VAR/HOB]	$38.4^b \pm 1.3$		39.4 ± 1.7	$34.4^c \pm 2.2$	
in 2 M Na_2CO_3 [84VAR/HOB]	$37.2^b \pm 1.2$		38.2 ± 1.7	$31.2^c \pm 2.1$	
$\lg\beta°_{3V}$	$6.9^c \pm 0.3$	$5.52^d \pm 0.33$		$4.9^c \pm 0.8$	$4.2^c \pm 1.2$
$\lg\beta°_{5IV} - \lg\beta°_{3V}$	$27.1^e \pm 0.7$	33.6 ± 3.7		$27.3^e \pm 1.5$	$23^g \pm 2$
$\lg\beta°_{3III} - \lg\beta°_{5IV}$			-22.5 ± 2.7	$^h\pm$	
from [84VAR/HOB]1M K_2CO_3			-22.1 ± 2.7		
from [84VAR/HOB]2M Na_2CO_3			-21.2 ± 3.5		
$\lg\beta°_{3III} - \lg\beta°_{3V}$		$11.2^f \pm 1.8$		$^e\pm$	$9.8^e \pm 1.5$

[a] [95SIL/BID] THE WORK FROM [83BOU/GUI] ALREADY REVIEWED IN [87ROB] SHOULD HAVE BEEN USED TO PROPOSE MORE COMPLEXATION CONSTANTS, [b] [92GRE/FUG] recalculated using the $\varepsilon(CO_3^{2-}, Na^+)$ value selected in this review, [c] [92CAP] THE Pu VALUE MUST BE REVIEWED AND HÉLÈNE CAPDEVILA IS RECALCULATING IT FROM HERE ORIGINAL DATA, FOR PUBLICATION, [d] this review, [e] calculated from the other values of this table, [f] using analogy, the expected value is 8.5±2.0, [g] [83BOU/GUI] measured the redox potential of the Am(IV)/Am(III) couple in concentrated carbonate media, this was reinterpreted in [87ROB] but the standard potential (in non complexing medium) of this couple is quite inaccurate, [h] THE Pu $\beta°_{3III}\ /\ \beta°_{5IV}$ VALUE COULD BE DEDUCED FROM THE SHIFT BETWEEN THE FORMAL AND THE STANDARD POTENTIAL OF THE Pu(IV)/Pu(III) REDOX COUPLE, [i] this value is much too low (see text).

2.5.2. Possible interpretation of the Np(V)/Np(IV) formal potential

The standard potential of the NpO_2^+/Np^{4+} couple, the stoichiometry and the stability of the limiting complex of Np(V), $NpO_2(CO_3)_3^{5-}$, are well established. It is then a good idea to deduce the stability of the limiting complex of Np(IV) from redox measurements in concentrated carbonate media; but more precise measurements are needed. We still try further calculations. For this we assume, that the potential was controlled by the two limiting complexes, $NpO_2(CO_3)_3^{5-}$ and $Np(CO_3)_5^{6-}$ (see the discussion on [81WES/SUL] in this appendix). The equilibrium would then be written

$$NpO_2(CO_3)_3^{5-} + e^- + 2\ CO_2 \Leftrightarrow Np(CO_3)_5^{6-}$$

The concentrations of the major species are not much affected by penetration of the air into the solution; but $\log_{10}P_{CO_2}$ is increased by 2.78 unit. This increases the redox potential of the solution by up to 330 mV, and induces an error of up to 5.6 orders of magnitude, on the determination of the formation constant of $Np(CO_3)_5^{6-}$. We use 0.2 V uncertainty on the formal potential of Fedoseev, Peretrukhin et col.: 0.1 V for the unstability of the measurement as the authors seem to have estimated and 0.1 V for possible junction potential.

Assuming equilibrium with the air, using $\varepsilon(Np(CO_3)_5^{6-}, Na^+) = 0.45 \pm 0.7$ (TO BE RECALCULATED FROM [95DEL]) and the standard potential of the NpO_2^+/Np^{4+} couple selected in this review (IT SHOULD BE

GIVEN AND DISCUSS IN CHAPTER VI.2.2), we estimate $\log_{10}\beta°_3((NpO_2(CO_3)_3^{5-})/\beta°_5(Np(CO_3)_5^{6-}))$ = 33.6 ± 3.7 (Table [79FED/PER]-2), and then using the formation constant of $NpO_2(CO_3)_3^{5-}$ selected in this review (chapter VI.6.1.1.2), we calculate $\log_{10}\beta°_5 = 39.2 \pm 3.7$ and in 1 M Na_2CO_3 $\log_{10}\beta'_5 = 41.5 \pm 3.4$. The β_5 values are discussed below. The uncertainty is mainly due to the inaccuracy of the Np(V)/Np(IV) measurement (see above) and of the $\varepsilon(Np(CO_3)_5^{6-}, Na^+)$ value.

2.5.3. Possible interpretation of the Np(IV)/Np(III) formal potential

Fedoseev and Peretrukhin also measured the formal potential of the Np(IV)/Np(III) couple at a dropping mercury electrode in 1 M K_2CO_3 solution. They propose -1.32 V at 25° C. This value has been confirmed later [84VAR/HOB]. The uncertainty must be quite important, since "all the waves [of Np and Pu(IV)/(III)] in carbonate media are irreversible". There is no information on the liquid junction potential, we then use 0.1 V uncertainty except for certain calculations, where junction potential cancels (assuming, that it was the same as in the measurement of the formal potential of the Np(V)/Np(IV) couple). By analogy with Am(III) [95SIL/BID], and with the same hypothesis as above, we assume that the Np(IV)/Np(III) redox equilibrium can here be written

$$Np(CO_3)_5^{6-} \Leftrightarrow Np(CO_3)_3^{3-} + e^- + 2\ CO_3^{2-}$$

The air penetration in a 1 M K_2CO_3 solution has little influence on $[CO_3^{2-}]$ (Table [79FED/PER]-1) and then on this equilibrium. We estimate the needed specific interaction coefficients from analogy with Am(III): $\varepsilon(Np(CO_3)_3^{3-}, K^+) = -0.11 \pm 0.25$, and with U(IV) and Pu(IV): $\varepsilon(Np(CO_3)_5^{6-}, K^+) = 0.45 \pm 1.0$. We increase the uncertainties, since we are using analogies, and it is known, that the redox behaviour of actinides can be slightly different in concentrated K_2CO_3 solutions from Na_2CO_3 ones; this is certainly due to ion pairing of highly negatively charged (-5 and -6) carbonate complexes, with Na^+ or K^+. Using the standard potential of the Np^{4+}/Np^{3+} redox couple selected in this review (chapter VI.2.3), we calculate $\log_{10}\beta°_5((Np(CO_3)_5^{6-}))/\beta°_3(Np(CO_3)_3^{3-}) = 22.5 \pm 2.7$. The uncertainty is again mainly due to the junction potential and to the $\varepsilon(Np(CO_3)_5^{6-}, K^+)$ value. We assume, that the $\beta°_3(An(CO_3)_3^{3-})$ value is not much different for Np and [95SIL/BID] Am: $\log_{10}\beta°_3(Np(CO_3)_3^{3-}) \approx 14.0 \pm 1.5$. Finally $\log_{10}\beta°_5(Np(CO_3)_5^{6-}) \approx 36.5 \pm 3.1$ and in 1 M K_2CO_3 $\log_{10}\beta'_5(Np(CO_3)_5^{6-}) = 39.7 \pm 1.7$. The β_5 values are discussed below.

From the measurements of the two formal potentials, we calculate $\log_{10}\beta°_3((Np(CO_3)_3^{3-})/\beta°_3(NpO_2(CO_3)_3^{5-}))$ = 11.2 ± 1.8 and then $\log_{10}\beta°_3(Np(CO_3)_3^{3-}) = 5.6 \pm 1.8$, where we now suppose, that the uncertainty due to the liquid junction cancels. This value is much too low, it is discussed below.

2.5.4. Discussion of the possible interpretations

The Np value of $\beta°_{3III}$ / $\beta°_{3V}$is calculated from the two measurements of Fedoseev, Peretrukhin et col.: it is a good indication of the internal consistency of their work because the major uncertainty cancels (liquid junction and stability of the limiting complex of Np(IV)). They are just (Table [79FED/PER]-2) in agreement with the one estimated (using the analogy between Np(III) and Am(III)). Still Am $\beta°_{3V}$ value is not a measurement. So we can only conclude, that the redox potentials measured by the authors have reasonable values, and that the limiting complexes of Np(III) and Am(III), seem to have the same stoichiometry and similar stability. The same conclusion also stands for Np(V) and Am(V). If we propose $\log_{10}\beta°_3 = 5.6 \pm 3.1$ for Np(III), where the uncertainty has been increased because in the table [79FED/PER]-2 we minimise it (to test consistency), the limiting complex of Np(III) would seem to be less stable than the Am(III) one. The opposite situation is rather expected. We then do not propose this value.

The two values calculated for the limiting complex of Np(IV) (table [79FED/PER]-2) are consistent. Since they now include the major uncertainties, this is quite expected. They have reasonable values, when compared with the U(IV) and Pu(IV) ones (table [79FED/PER]-2). The value calculated from the potential of the Np(V)/Np(IV) couple, might be too high: this can be attributed to the large inaccuracy of the measurement. This could also be attributed to an error in our interpretation: the formation of a new complex containing some Np(IV). There is no spectrophotometric evidence of such a new complex of pure Np(IV) (see the discussion of [81WES/SUL] in this appendix). A mixed Np(V)-Np(IV) complex might then be formed, this very doubtful explanation is evoked elsewhere in this appendix [84VAR/PER] only because it cannot be eliminated, not because there is any strong evidence of it. We then do not propose the value calculated from the potential of the

Table [85RAI/RYA]-1 Speciation in 0.01 M carbonate solutions, calculated with the parameters of the tables [71MOS5]-1a and b. M is the initial concentration of $NaHCO_3$. lg is $\log_{10}$. The definitions of the constants are in table [71MOS5]-1b (name); but they are here in molar (and not molal) units. NaOH was added to a 0.01 M $NaHCO_3$ solution, the pH was measured. The first line is the speciation without any NaOH addition, we assume, that the difference between the two first lines is the uncertainty for the calculations of the table [85RAI/RYA]. Speciation is used in this appendix to draw the figures and to perform the calculations.

M	$\lg P_{CO_2}$	$\lg[CO_3^{2-}]$	$\lg[HCO_3^-]$	$\lg[Na^+]$	I	$\lg[CO_2]$	$\lg[OH^-]$	lg k'$_1$	lg k'$_{1,2}$	lg k'$_{p1}$	pH	$\lg a_{CO_3^{2-}}$	$\lg a_{OH^-}$
0.01	-2.48	-3.96	-2.01	-2.00	0.01	-3.95	-5.71	-3.76	-7.65	-6.18	8.24	-4.14	-5.76
0.01	-3.15	-3.31	-2.02	-1.98	0.01	-4.62	-5.05	-3.76	-7.65	-6.18	8.9	-3.50	-5.10
0.01	-4.61	-2.33	-2.28	-1.83	0.02	-6.08	-3.84	-3.79	-7.65	-6.18	10.1	-2.56	-3.90
0.01	-5.09	-2.19	-2.45	-1.78	0.02	-6.56	-3.54	-3.80	-7.65	-6.18	10.4	-2.44	-3.60
0.01	-6.18	-2.05	-2.93	-1.70	0.03	-7.65	-2.93	-3.81	-7.65	-6.18	11	-2.33	-3.00
0.01	-7.97	-2.01	-3.81	-1.53	0.04	-9.44	-2.02	-3.83	-7.65	-6.18	11.9	-2.32	-2.10
0.01	-8.49	-2.00	-4.08	-1.43	0.05	-9.96	-1.77	-3.84	-7.65	-6.18	12.15	-2.34	-1.85
0.01	-10.14	-2.00	-4.94	-0.91	0.13	-11.61	-0.99	-3.93	-7.66	-6.19	12.9	-2.49	-1.10
0.01	-11.56	-2.00	-5.72	-0.34	0.47	-13.03	-0.36	-4.08	-7.67	-6.20	13.5	-2.72	-0.51
0.01	-12.30	-2.00	-6.13	-0.05	0.91	-13.77	-0.06	-4.19	-7.69	-6.22	13.8	-2.86	-0.21

Table [85RAI/RYA]-2 Calculation of the maximum value of the formation constant of some complexes of Np(IV) from the [85RI/RYA] solubility measurements and comparison with the values proposed in the literature or calculated in this review, and with the know ones for U [92GRE/FUG] and Pu [92CAP]. The $\log_{10}$ of the maximum value of the $Np(CO_3)_i(OH)_j^{4-2i-j}$ formation constant, β_{ij}, is $\log_{10}\beta_{ij} = \log_{10}[Np(IV)] - \log_{10}Ks - i \log_{10}[CO_3^{2-}] + (4-j) \log_{10}[OH^-]$. Among the proposed Np(IV) complexes proposed in the literature, only the observations of the formation of $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ seem believable.

	Np $\log_{10}\beta_{ij}$ upper limit [85RAI/RYA]	this review	$\log_{10}\beta_{ij}$ values U	Pu	Np	references for Np
$\lg{}^*\beta_5$	-24.7	-25.5				
$\lg\beta_1$	22.5	30.4				
$\lg\beta_2$	27.9	33.1				
$\lg\beta_3$	33.2	35.8			37 ± 1.2	[89MOR/PRA]
$\lg\beta_4$	38.5	38.4	35.12	33.2	41.1 ± 1.4	[89MOR/PRA]
$\lg\beta_5$	41.6	40.7	34	32.2	39.1 ± 3.7	calculated from [79FED/PER] E(V/IV)
					36.4 ± 3.1	calculated from [79FED/PER] E(IV/III)
$\lg\beta_{22}$		41.9			45.69± 0.44	[90PRA/MOR]
$\lg\beta_{24}$		47.8			53.07± 0.44	[90PRA/MOR]
$\lg\beta_{14}$		46.5			53.05± 0.02	[71MOS5]

other upper limits of Np $\log_{10}\beta_{ij}$ values

i,j	2,2	2,4	1,4	5,0	4,0	3,0	2,0	1,0	5,1	4,1	3,1	2,1	1,1
	42	48	46	41	38	36	33	30	44	42	40	37	35
i,j	0,1	4,2	3,2	1,2	0,2	4,3	3,3	2,3	1,3	0,3	4,4	3,4	0,5
	32	45	44	39	37	48	47	45	44	41	51	49	44

Np(V)/Np(IV) couple. We do not either propose the one calculated from the potential of the Np(IV)/Np(III) couple, because it relies on an analogy between Am(III) and Np(III).

Our calculations finally show, that our hypothesis and the numerical values measured by Fedoseev and Peretrukhin are reasonable; there is too much inaccuracy in this work, there are some problems with the methodology and too few experimental details. For this, we cannot be sure whether our main hypothesis (stoichiometry of the limiting complex of Np(IV)) is correct or not, and we cannot deduce any thermodynamic data from this work. THIS CONCLUSION COULD BE RE DISCUSSED AFTER THE RESULT OF THE Pu REVIEW. UP TO NOW, THERE ARE SOME DIFFERENCES BETWEEN THE I CORRECTIONS FOR U AND Pu. THIS COULD BE ATTRIBUTED TO ION PAIRING. THIS INDUCES SIGNIFICANT DIFFERENCES IN THE VALUES OF THE FORMAL FORMATION CONSTANTS OF THEIR LIMITING COMPLEX. CALCULATIONS USING A LIMITING COMPLEX WITH 6 CARBONATES SHOULD ALSO BE TRIED (EVEN IF THERE IS NO EVIDENCE OF SUCH COMPLEX).

2.6. [81WES/SUL]

Wester, D.W., Sullivan, J.C. *Electrochemical and spectroscopic studies of neptunium(IV), -(V), -(VI) in carbonate-bicarbonate buffers*, J. Inorg. Nuclear Chem., 43 11 (1981) 2919-2923.

Np(V) was electrolysed in 1 M carbonate and in 1 M bicarbonate solutions by controlled electrolysis at -1.8 V to produce Np(IV). Water was certainly also partially reduced (see [95DEL] and the discussion of [84VAR/HOB] in this appendix); this (see [95DEL] and the discussion of [84VAR/HOB] in this appendix) produced OH^-: pH (and then $[CO_3^{2-}]$) might then have been greater than its initial (theoretical)value. Still, it was measured (see below); but this measurement possibly included some junction potential contribution since the ionic medium was controlled by reactive species, this contribution was probably quite a small correction (see [95DEL]); but it might have been enough to change the final spectrum since a later work [95DEL] shows (as for Pu(IV) [92CAP]), that the dissociation of the limiting complex could start approximately in these conditions. The use of only a platinum electrode is reported for electrolysis; but certainly a Hg electrode was used. The same methodology will be used later to prepare Np(IV) successfully [79FED/PER] [95DEL], or with some difficulties [84VAR/HOB] [93LI/KAT]. One Np(IV) absorption spectrum in 1 M $NaHCO_3$ or Na_2CO_3 solution is reported. It does not vary from pH 8.3 to 11.2. Our calculated pH values are 7.9 and 11.7. pH is shifted in two different directions: it then cannot only be attributed to a systematic calibration deviation (junction potential, activity coefficients); but it could possibly be attributed to CO_2 penetration into the Na_2CO_3 solution or/and water reduction during electrolysis in the $NaHCO_3$ one. It is the same as the ones reported elsewhere [77SAI/UEN] [84VAR/HOB] [93LIT/KAT] [95DEL] in concentrated carbonate media. This is an evidence, that a limiting complex is formed in theses conditions. The measurement by Fedosseev, Peretrukhin et col. [79FED/PER] were also performed in these conditions (Figure [71MOS5]-2). No thermodynamic data and no stoichiometry can de deduced from this work. Still, since the limiting complex is probably stable over nearly 3 pH units (this will be confirm later [95DEL]), this suggests, that this limiting complex does not include any OH^- ligand. We can indeed interpret all the spectrophotometric, redox and solubility measurements (figures [71MOS5], table [79FED/PER]-2) with such a complex: namely $Np(CO_3)_5^{6-}$ (by analogy with Ce(IV), Th, U(IV) and Pu(IV)). As for the limiting complex of U(IV) [92GRE/FUG] and Pu(IV) [92CAP] it is dissociated when decreasing the ionic strength (see [95DEL] and the reinterpretation of [93LI/KAT] in this appendix).

2.7. [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.

See [84VAR/HOB]

2.8. [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.

The preparation of Np(IV) in carbonate solution, the absorption spectrum and the electrochemical measurements are repetitions and confirmations of previous works[79FED/PER] [81WES/SUL]. We then performed the same calculation: see the analysis of [79FED/PER] in this appendix and the Table [79FED/PER]-2.

Cyclic voltammetry of Np(V) in 2 M Na_2CO_3 solution confirms the previous [79FED/PER] [81WES/SUL] electrochemical observations: the reduction of Np(V) is not reversible and is observed only at -1.7 V (at pH = 12.9), where [79FED/PER] Np(IV) is quantitatively reduced to Np(III). The reduction peak is shifted toward more negative values (-1.8 V) at $[OH^-]$ = 0.25 M, and its shape changes with a "pre-peak" at -1.63 V at pH = 10.9. This stabilisation of Np(V) can certainly be explained by the formation of a mixed OH-CO_3 complex of Np(V), for which some spectral evidence is shown in this publication, and was confirmed later [89RIG]. On the other end, the Np(IV) carbonate limiting complex is dissociated in $[OH^-]$ = 0.25 M media, at least by the formation of $Np(OH)_4^0$ (or its polymers).

Table [89MOR/PRA]-1 Speciation in NaOH solutions equilibrated with the air, calculated with the parameters of the tables [71MOS5]-1a and b. M is the total carbonate concentration. lg is $\log_{10}$. The definitions of the constants are in table [71MOS5]-1b (name); but they are here in molar (and not molal) units. The ionic strength was supposed to be constant (0.03 M), the pH was measured. The values, that do not change are in the first line. Speciation is used in this appendix to draw the figures and to perform the calculations.

M	$\lg P_{CO_2}$	$\lg[CO_3^{2-}]$	$\lg[HCO_3^-]$	$\lg[CO_2]$	$\lg[OH^-]$	$\lg k'_1$	$\lg k'_{1,2}$	$\lg k'_{p1}$	pH	$\lg a_{CO_3^{2-}}$	$\lg a_{OH^-}$
0.0098	-3.5	-2.83	-2.08	-4.97	-4.78	-4.02	-7.66	-6.19	9.10	-3.46	-4.91
0.0066		-3.13	-2.23	-4.97	-4.93				8.95	-3.76	-5.06
0.0058		-3.23	-2.28	-4.97	-4.98				8.90	-3.86	-5.11
0.0045		-3.43	-2.38	-4.97	-5.08				8.80	-4.06	-5.21
0.0028		-3.83	-2.58	-4.97	-5.28				8.60	-4.46	-5.41
0.0015		-4.33	-2.83	-4.97	-5.53				8.35	-4.96	-5.66
0.0014		-4.43	-2.88	-4.97	-5.58				8.30	-5.06	-5.71

The precipitation of Np(III) is evoked by the authors ; but as Am(III), Np(III) is quite soluble in this medium : $Np(OH)_3$ could still precipitate directly on the electrode, where the electrolysis of water can locally produce enough quantity of OH^- anion, this type of procedure is well known for electrodeposition on solid electrodes. This also explains, that the precipitate is re-dissolved in the bulk of the solution, when the electrolysis is stopped. It then cannot be evoked (as the authors do) in the other cases, where $Np(OH)_4$ can also precipitate (see below). The changes in the shape of the electrochemical peaks could be due to some side chemical reaction such as Np(III) + Np(V) → 2 Np(IV), precipitation of Np(IV) and/or formation of an intermediary complex as already evoked in this appendix [79FED/PER]. The authors had some difficulties to reduce by electrolyse their Np(V) solution, and to keep Np(IV) solution stable. As already explained (see the discussion on [79FED/PER] in this appendix) the poor stability of the potential can be due to penetration of carbonic gas into the solution. In addition, the water is also electrolysed during the preparation: this generates some OH^-, that also reacts with carbonic gas. A small increase of $[OH^-]$ should be enough to dissociate the carbonate limiting complex of Np(IV) (into $Np(OH)_4^0$ or another unknown Np(IV) complex containing some hydroxide anion), which results in the precipitation of Np(IV) solid hydroxide. In our opinion, this was clearly the case during this work (from the description of the experimental procedure and the difficulties reported by the authors, and it was confirmed later [95DEL]); but the authors did not mention it in their interpretation, and conclude, that they have not confirmed the previous work of Wester and Sullivan [81WES/SUL]. For the reason explained above, we do not accept this conclusion, and we are not certain, that the authors clearly understood the major chemical reactions involved in their Np(IV) preparation. Finally no thermodynamic data can be deduced from the Np(V)/Np(IV) or Np(IV)/Np(III) studies. No new piece of information on Np(IV) nor Np(III) is shown in this work.

2.9. [85RAI/RYA]

Rai, D., Ryan, J.L. *Neptunium(IV) hydrous oxide solubility under reducing and carbonate conditions, Inorg. Chem.*, 24 (1985) 247-251.

The authors give convincing evidences, that some published formation constant of the Pu(IV) carbonate complexes $PuCO_3^{2+}$ through $Pu(CO_3)_5^{6-}$ [58MOS/GEL] [83KIM/LIE], and of the Np(IV) carbonate complex $Np(OH)_4CO_3^{2-}$ [71MOS5] are much too high to be "believable". This review accepts these conclusions. (Pu?). To confirm this, the authors decided to show, that Np(IV) solubility is not increased by the formation of any new soluble complex, when the carbonate concentration of the solution is increased to up to 0.01 M at various pH. The methodology and the interpretation are correct, we then agree with their conclusions. It agrees with our reinterpretation (see the discussion on [71MOS5] in this appendix), that predicts the formation of negligible quantity of Np(IV) carbonate complex in these experimental conditions.

THIS § SHOULD RATHER BE INCLUDED IN THE DISCUSSION OF HYDROLYSIS. A strong reducing agent where used: $Na_2S_2O_4$, Fe or Zn, "that in general maintained redox potentials closed to the boundary at which water is reduced to produce H_2". In other cases, $10^{-4.4}$ to $10^{-7.5}$ M solubility was found and attributed to Np(V) or Np(VI). As usually (see chapter???) the Np(IV) solubility is found to be a little less than 10^{-8} M: $10^{-7.7}$ to $10^{-8.45}$ M. Its mean value and 1.5 standard deviation are $10^{-8.26\pm0.39}$ M. According to the authors, these solubility results are below or near the detection limit: $10^{-8.3}$ M obtained using liquid scintillation. This is a good value for this method. The ^{237}Np decays into ^{233}Pa, that could interfere, this problem is not evoked. U(IV) and Pu(IV) solubility's seem to be less than $10^{-8.3}$ M in these conditions: around 10^{-9}-10^{-10} M. Too few

Table [90PRA/MOR]-1 Speciation in 0.01 M carbonate solutions, calculated with the parameters of the tables [71MOS5]-1a and b. M is the initial concentration of $NaHCO_3$. lg is $\log_{10}$. The definitions of the constants are in table [71MOS5]-1b (name); but they are here in molar (and not molal) units. NaOH was added to a 0.01 M $NaHCO_3$ solution, the pH was measured. The two first lines are not calculated: the pH is less than the pH calculated in a 0.01 M $NaHCO_3$ solution without any NaOH addition. Speciation is used in this appendix to draw the figures and to perform the calculations.

M	$\lg P_{CO_2}$	$\lg[CO_3^{2-}]$	$\lg[HCO_3^-]$	$\lg[Na^+]$	I	$\lg[CO_2]$	$\lg[OH^-]$	lg k'$_1$	lg k'$_{1,2}$	lg k'$_{p1}$	pH	$\lg a_{CO_3^{2-}}$	$\lg a_{OH^-}$
											8.05		
											8.2		
0.01	-2.74	-3.71	-2.01	-1.99	0.01	-4.21	-5.46	-3.76	-7.65	-6.18	8.5	-3.89	-5.50
0.01	-2.94	-3.51	-2.02	-1.99	0.01	-4.41	-5.26	-3.76	-7.65	-6.18	8.7	-3.69	-5.30
0.01	-2.84	-3.61	-2.01	-1.99	0.01	-4.31	-5.36	-3.76	-7.65	-6.18	8.6	-3.79	-5.40
0.01	-3.47	-3.03	-2.04	-1.96	0.01	-4.94	-4.75	-3.77	-7.65	-6.18	9.2	-3.22	-4.80
0.01	-4.00	-2.64	-2.11	-1.91	0.01	-5.47	-4.30	-3.78	-7.65	-6.18	9.65	-2.85	-4.35
0.01	-4.06	-2.60	-2.13	-1.90	0.02	-5.53	-4.25	-3.78	-7.65	-6.18	9.7	-2.81	-4.30
0.01	-4.26	-2.49	-2.17	-1.87	0.02	-5.73	-4.10	-3.78	-7.65	-6.18	9.85	-2.71	-4.15
0.01	-4.77	-2.28	-2.33	-1.81	0.02	-6.24	-3.74	-3.79	-7.65	-6.18	10.2	-2.52	-3.80
0.01	-4.47	-2.39	-2.23	-1.85	0.02	-5.94	-3.94	-3.79	-7.65	-6.18	10	-2.62	-4.00
0.01	-4.47	-2.39	-2.23	-1.85	0.02	-5.94	-3.94	-3.79	-7.65	-6.18	10	-2.62	-4.00
0.01	-4.06	-2.60	-2.13	-1.90	0.02	-5.53	-4.25	-3.78	-7.65	-6.18	9.7	-2.81	-4.30
0.01	-5.09	-2.19	-2.45	-1.78	0.02	-6.56	-3.54	-3.80	-7.65	-6.18	10.4	-2.44	-3.60
0.01	-5.26	-2.16	-2.52	-1.76	0.02	-6.73	-3.44	-3.80	-7.65	-6.18	10.5	-2.41	-3.50
0.01	-5.44	-2.13	-2.59	-1.75	0.03	-6.91	-3.34	-3.80	-7.65	-6.18	10.6	-2.39	-3.40
0.01	-5.44	-2.13	-2.59	-1.75	0.03	-6.91	-3.34	-3.80	-7.65	-6.18	10.6	-2.39	-3.40
0.01	-5.44	-2.13	-2.59	-1.75	0.03	-6.91	-3.34	-3.80	-7.65	-6.18	10.6	-2.39	-3.40
0.01	-6.18	-2.05	-2.93	-1.70	0.03	-7.65	-2.93	-3.81	-7.65	-6.18	11	-2.33	-3.00
0.01	-6.18	-2.05	-2.93	-1.70	0.03	-7.65	-2.93	-3.81	-7.65	-6.18	11	-2.33	-3.00
0.01	-6.37	-2.04	-3.02	-1.69	0.03	-7.84	-2.83	-3.81	-7.65	-6.18	11.1	-2.32	-2.90
0.01	-8.18	-2.01	-3.92	-1.50	0.04	-9.65	-1.92	-3.83	-7.65	-6.18	12	-2.33	-2.00
0.01	-7.76	-2.01	-3.71	-1.56	0.04	-9.23	-2.13	-3.83	-7.65	-6.18	11.8	-2.31	-2.20
0.01	-8.59	-2.00	-4.13	-1.41	0.05	-10.06	-1.72	-3.84	-7.65	-6.18	12.2	-2.34	-1.80
0.01	-7.97	-2.01	-3.81	-1.53	0.04	-9.44	-2.02	-3.83	-7.65	-6.18	11.9	-2.32	-2.10
0.01	-8.59	-2.00	-4.13	-1.41	0.05	-10.06	-1.72	-3.84	-7.65	-6.18	12.2	-2.34	-1.80

experimental details are given on pH measurement (which pH buffers are used for calibration? Is the junction potential taken into account? Is it really pH or $-\log_{10}[H^+]$?); but this would have little effect here. Not any new thermodynamic data can be proposed from this work, but the authors had the good idea to calculate the maximum values of the formation constants of some Np(IV) complexes, that were not detected during their solubility measurement. We verify these calculations and find the same results.

To estimate the maximum value of the formation constant, $\beta_{i,j}$, of the complex $Np(OH)_i(CO_3)_j^{4-i-2j}$, one can assume, that the solubility, S, is approximately $[Np(OH)_4^0]$, and $[Np(OH)_i(CO_3)_j^{4-i-2}]$ / $[Np(OH)_4^0]$ is less than, e, the relative uncertainty on S: $e + (4 - i)\log_{10}[OH^-] - j \log_{10}[CO_3^{2-}] \geq \log_{10}\beta_{i,j} - \log_{10}\beta_{4,0}$. Another possibility is to assume, that S is more than $[Np(OH)_i(CO_3)_j^{4-i-2}]$: $\log_{10}S + (4 - i)\log_{10}[OH^-] - j \log_{10}[CO_3^{2-}] \geq \log_{10}\beta_{i,j} + \log_{10}Ks_0$, and compare it with the stability of the major Np(IV) soluble complex: $Np(OH)_4^0$. $^*\beta_{4,0}/^*\beta_{i,j}$ is then calculate. The two methods are practically equivalent since in these conditions, $S \approx Ks_0\ \beta_{4,0}$, and $\beta_{4,0}$ has not been directly measured: it is always deduced from the direct measurement of $^*Ks_0\ ^*\beta_{4,0}$ and $^*Ks_0$. We calculate the possible maximum value of $\beta_{i,j}$ (table [85RAY/RIA]-1) from $^*Ks_0\ ^*\beta_{i,j}$, using the [85RAY/RIA] value of $Ks_0 = -53.5$ as it is certainly done in [85RAY/RIA]. These calculations show, that among the proposed Np(IV) complexes proposed in the literature, only the observations of the formation of $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ are believable.

2.10. [86PRY/REE]

Pryke D. C., Rees J. H. *Understanding the behaviour of the actinides under disposal conditions: a comparison between calculated and experimental solubility's*. Radiochim. Acta 40 (1986) 27-32.

The solubility of some actinides was measured in "simulated pore water [...] prepared by equilibrating demineralised water with crushed concrete for several months. [...] The pH was varied by addition of sodium

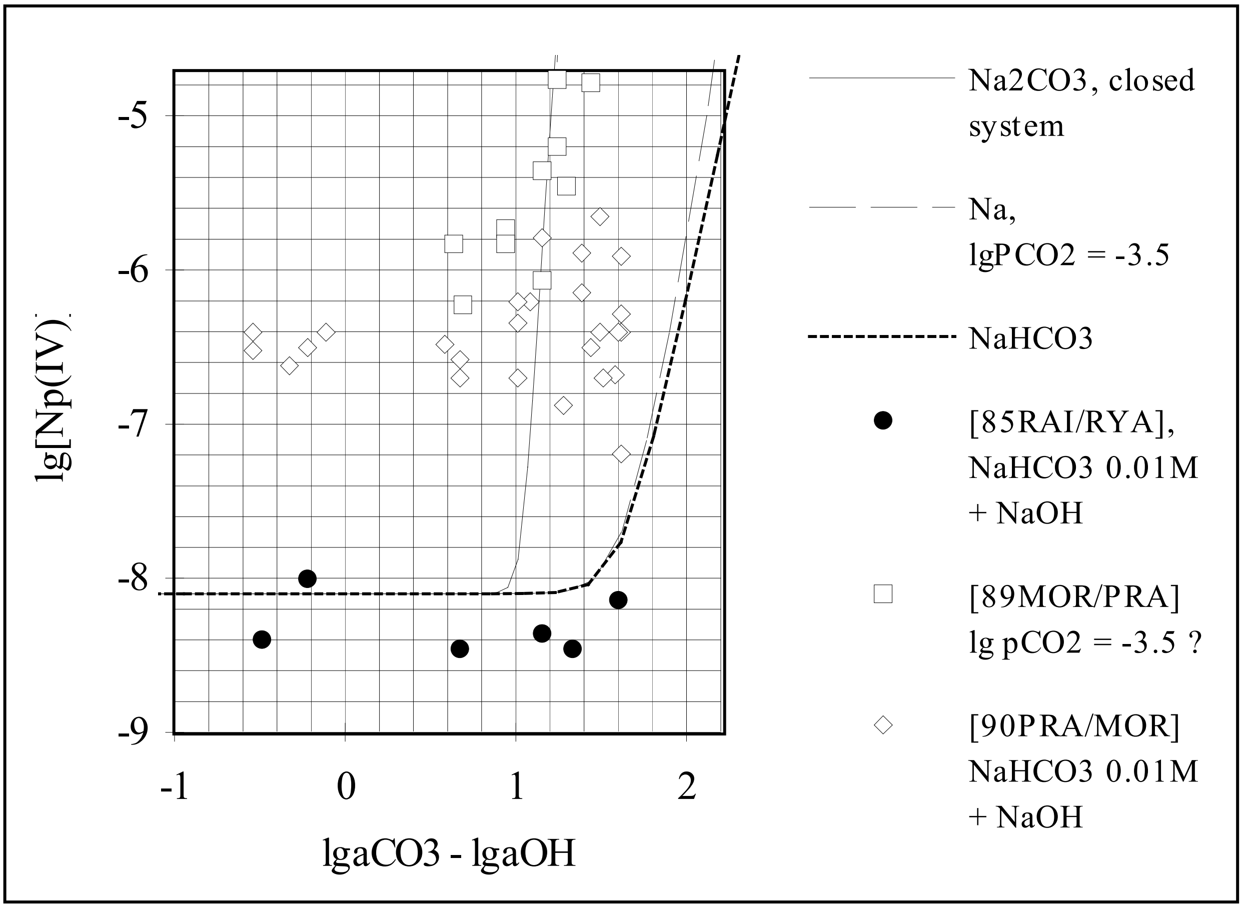


Figure [90PRA/MOR]-1: Np(IV) solubility in carbonate media. This figure is a detail of the figure [71MOS5]-3. The cited authors (experimental points in the figure) assume, that the solid phase is NpO_{2s} or $Np(OH)_{4s}$. When the predominating soluble complex is $Np_k(CO_3)_i(OH)_j^{4k-2i-j-}$, the Np(IV) solubility, S, is $\log_{10}S = k \log_{10}Ks° + \log_{10}(k\ \beta_{ijk}) + i \log_{10}a_{CO_3^{2-}} - (4k - j)\log_{10}a_{OH^-})$ All the experimental points would then have fallen on the same line, if the major soluble complex had the stoichiometry i = 4k - j, typically $Np(CO_3)_2(OH)_2^{2-}$ (proposed in [90PRA/MOR]) or $Np(CO_3)_4^{4-}$ (proposed in this review). The experimental data of Prapoto's thesis [89MOR/PA] [90PRA/MOR] are too scattered to make a conclusion. aX is the activity of X (mole/kg).

hydroxide or hydrochloric acid." According to the chemical analysis of the water at pH 12, $[CO_3^{2-}]$ was 30 µM. This value might be too high for a water equilibrated with cement [90VIT]. The results are consistent with a previous one [85RAI/RYAN]; but solubility is measured and found constant up to a higher pH, and $[CO_3^{2-}]$ is here lower. For this last reason we do not use this work to estimate maximum values of formation constants of Np(IV) carbonate complexes (see the discussion on [85RAI/RYAN] in this appendix).

If the results of Np(IV) solubility are really above the detection limit, the behaviour of Np(IV) and Pu(IV) are slightly different: Pu(IV) solubility is smaller and it increases at pH 13.

2.11. [89MOR/PRA]

Moriyama H., Pratopo M. I., Higashi K. *The solubility and colloidal behaviour of neptunium(IV).* Sci. total environment, 83 (1989) 227-237.

This publication is the chapter 2 of Prapoto's thesis. It seems to be a first try to perform the same type of experiment as [85RAI/RYAN]; but the results are less accurate. The critical bibliographic discussion of [85RAI/RYAN] was cited, but not used. The experimental procedure used to prepare the solutions, and to perform the solubility measurements led to the non reversible formation of Np(IV) hydroxide, that precipitates and gives particles (or colloids). Despite what is said in this publication, the formation of colloids is not controlled, and its effect on the solubility is not quantitatively understood. This type of reaction is well known for a long time (see the discussion of [71MOS5] in this appendix); and is usually unwanted and uncontrolled. The authors say, that they maintained constant ionic strength, and that they have added NaOH (this might not be consistent) to adjust the pH (its variations were probably due to penetration of the carbonic gas of the air). Assuming the achievement of equilibrium with the air, and that they effectively used this procedure (but it is not clear and this cannot be checked), we have calculated the speciation (Table [89MOR/PRA]-1). There are also some uncertainties in this calculation since we do not know how the glass electrode was calibrated

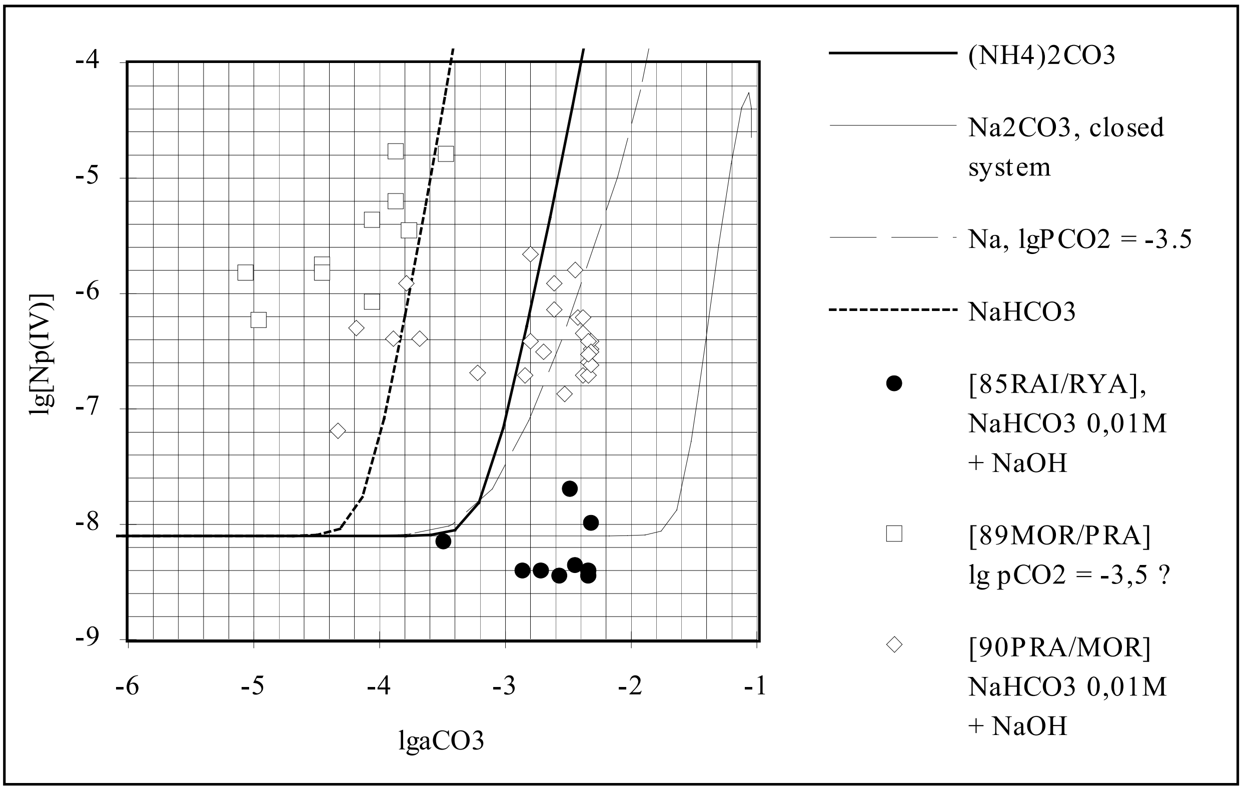


Figure [90PRA/MOR]-2: Np(IV) solubility in carbonate media. This figure is a detail of the figure [71MOS5]-3, and is similar to the figure [90PRA/MOR]-1. The cited authors (experimental points in the figure) assume, that the solid phase is NpO_{2s} or $Np(OH)_{4s}$. When the predominating soluble complex is $Np_k(CO_3)_i(OH)_j^{4k-2i-j-}$, the Np(IV) solubility, S, is $\log_{10}S = k \log_{10}Ks° + \log_{10}(k\ \beta_{ijk}) + (\log_{10}a_{CO_3^{2-}} - (4k - j) \log_{10}a_{OH^-})$. All the experimental points would then have fallen on the same line, if the major soluble complex had the stoichiometry j = 4 / k, typically $Np(OH)_4^0$, $Np(OH)_4CO_3^{2-}$ (proposed in [71MOS5]) or $Np(OH)_4(CO_3)_2^{4-}$ (proposed in [90PRA/MOR]). The experimental data of Prapoto's thesis [89MOR/PA] [90PRA/MOR] are too scattered to make a conclusion.

(junction potential? pH or -$\log_{10}[H^+]$?). The solubility data (Figures [71MOS5]-3 and [90MOR/PRA]-1) are higher than the well established (see the discussion on [85RAI/RYAN]) solubility of Np(IV) in these chemical conditions. The highest solubility values are obtained in contact with the air; but no Np(V) was found in the solution. The non reversible reactions mentioned above are enough to explain this discrepancy. No thermodynamic data can then be deduced from this work. For the same reason, no stoichiometry of the soluble species can be deduced. Still, it seems, that the solubility increase with $[CO_3^{2-}]$ is significant . Even if we assume, that this is not due to the formation of Np(V) in contact with the air (see above), this cannot exactly be attributed to the formation of $Np(CO_3)_4^{4-}$ or $Np(CO_3)_5^{6-}$ (Figure [71MOS5]-3). The systematic error on the pH measurement, mentioned above, is enough to explain this discrepancy; we cannot then conclude, that it is an evidence of the formation of some unknown complex. Finally the authors propose some curve fitting to interpret their results without any sensitivity analysis: many soluble carbonate or hydroxide complexes can be used to fit those results, that are hardly correlated to any chemical parameter in such a narrow domain of chemical conditions (Figures [90PRA/MOR]-1 and 2).

In addition, as already said above, they did not prepare correctly their solid phase: this problem is known from a long time (see the discussion on [71MOS5] in this appendix). They also probably did not maintain correctly their reducing conditions. They used their formation constants in many other works [89PRA/MOR] [89TAN/NAG] [90PRA/MOR] [91ITA/TAN] [93PRA/YAM], that should then be reinterpreted. In addition, in many of these works, the chemical conditions are not correctly controlled and the reproducibility is not checked. Even the literature cited by the authors (specially [85RAI/RYAN]) already pointed out that this type of methodology, interpretations and results should be avoided.

2.12. [89TAN/NAG]

Tanaka, S., Nagasaki, S., Itagaki, H., Yamawaki *Speciation and retardation phenomena of neptunium in underground environments. In High level radioactive waste and spent fuel management*. Slate S.C., Kohout, R. Suzuki, A. ed. (1989) vol 2, 375-381.

Table [93LI/KAT]-1 Speciation in Na_2CO_3 solutions, calculated with the parameters of the tables [71MOS5]-1a and b. M is the initial concentration of Na_2CO_3. lg is $\log_{10}$. The definitions of the constants are in table [71MOS5]-1b (name); but they are here in molar (and not molal) units. NaOH was added to a 0.01 M $NaHCO_3$ solution, the pH was measured. We assume, that the solutions were equilibrated with the air. Speciation is used in this appendix to draw the figures and to perform the calculations.

M	$\lg P_{CO_2}$	$\lg[CO_3^{2-}]$	$\lg[HCO_3^-]$	$\lg[Na^+]$	I	$\lg[CO_2]$	$\lg[OH^-]$	$\lg k'_1$	$\lg k'_{1,2}$	$\lg k'_{p1}$	pH	$\lg a_{CO_3^{2-}}$	$\lg a_{OH^-}$
0.20	-2.45	-0.79	-1.13	-0.40	0.56	-3.92	-3.75	-4.09	-7.67	-6.20	10.1	-1.54	-3.91
1.00	-2.48	-0.05	-0.69	0.30	2.90	-3.95	-3.80	-4.45	-7.75	-6.28	10.1	-1.16	-3.94
1.00	-3.18	-0.01	-1.36	0.30	2.98	-4.65	-3.10	-4.45	-7.75	-6.28	10.8	-1.13	-3.24

Table [93LI/KAT]-2 Estimation of the dissociation constant of the limiting complex, calculated from the spectrum of An(IV), Np(IV) in 0.2 M Na_2CO_3 solution at pH 10.1. $K_5 = [Np(CO_3)_5^{6-}] / [Np(CO_3)_4^{4-}]/[CO_3^{2-}]$

An	$\lg K_5°$	+/-	Δε	+/-	$\lg K_5$	+/-	reference
U	-1.12	0.25	-0.13	0.11	1.81	0.25	[92GRE/FUG]
Np	-1.43	0.56	0.385	0.62	1.29	0.50	calculated (by this review) [93LI/KAT]
Pu	-1.0	0.2	0.90	0.10	1.51	0.20	[92CAP]

This is a sorption and migration work on Np(IV). No thermodynamic data can be deduce from this work. It uses erroneous chemical speciation from [88NAG/TAN].

2.13. [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.

It is the chapter 3 of Prapoto's thesis. It is an unsuccessful try to exactly duplicate [85RAI/RYAN] experiments. Experimental results are not much consistent with the chapter 2 [89MOR/PRA] of the thesis, and are higher (Figure [71MOS5]-3 we have calculate the speciation to plot the points on this figure) than the well established [85RAI/RYAN] solubility in these conditions (see the discussion of [85RAI/RYAN] in this appendix). The same type of experimental errors and incorrect curve fitting as in chapter 2 are made: no thermodynamic data should be deduced from these measurements, that are scattered, probably out of equilibrium, and where the solid phase might vary during the measurements. The stoichiometry and the formation constants proposed by the authors (table [85RAI/RYAN]) are then not considered in this review.

2.14. [93LI/KAT]

Li, Y., Kato, Y., Yoshida, Z. *Electrolytic preparation of neptunium species in concentrated carbonated media.* Radiochim. Acta 60 (1993) 115-119.

Np(III), Np(IV), Np(V) and Np(VI) are prepared by electrolysis in 1 M $HClO_4$ (HEINO SHOULD CHECK, WETHER THE MEASURED E DURING THE ELECTROLYSIS ARE CONSISTENT WITH THE VALUES PROPOSED IN THIS REVIEW). This way of preparation is well known for a long time. The same type of electrolysis is done in 1 M Na_2CO_3 solutions. The Np(VI)/Np(V) reasonably reversible couple has been studied for a long time. The preparation of Np(IV) is possible [79FED/PER] [81WES/SUL] [84VAR/HOB] [95DEL]; but Li, Kato et col. did not succeed, because the potential was not negative enough, probably because they did not use a proper electrode. The redox study is then not much useful and it is not very precise since there is no indication on the junction potential.

Np(IV) carbonate complex was obtained by mixing a Np^{4+} acidic solution with a Na_2CO_3 solution. The spectrum of the solution is the well known [71MOS5] [77SAI/UEN] [81WES/SUL] [84VAR/HOB] [95DEL] spectrum of the limiting carbonate complex of Np(IV); but for the first time, the spectrophotometric evidence of the dissociation of the Np(IV) limiting complex is shown, when the pH is decreased. These spectra have been confirmed later [95DEL]. This occurs in similar conditions as for U [92GRE/FUG] and Pu [92CAP]. This again suggests the same interpretation as for these actinides(IV):

$$Np(CO_3)_5^{6-} \rightarrow Np(CO_3)_4^{4-} + CO_3^{2-}.$$

We estimate, that the published spectrum probably corresponds to less than 50 % (10 %? BETTER ESTIMATION OF THIS % CAN BE MADE, IT SHOULD BE IN THE NEXT VERSION OF THIS

APPENDIX, AFTER THE REVIEWING OF [95DEL]) of the above reaction and we estimate the constant of this equilibrium (table [93LI/KAT]-2).

2.15. [95DEL]

Delmau L. *Np(IV) en solution carbonate concentrée.* Note technique CEA à paraître. (1995 vraisemblablement).

THIS REPORT WILL BE REVIEWED WHEN IT WILL BE PUBLISHED. Np(IV) Na_2CO_3 solutions were prepared by electrolysis on a Hg electrode as [81WES/SUL] and [84VAR/HOB]; but careful observations give very interesting qualitative results, that confirm the discussion of [84VAR/HOB] in this appendix. Np(IV) was controlled spectrophometrically (after dilution in acidic medium, where Np(V) impurity can more easily be detected). Np(V) could be electrolysed to Np(IV) in 1.5 M Na_2CO_3 solution, only simultaneously to water reduction: pH increase is indeed measured. If the potential is not enough negative, Np(IV) starts to precipitate even before the total reduction of the Np(V) solution : a white precipitate is formed at pH higher than 12.7. The initial pH was 11.52 (close enough to the theoretical one). The initial yellow colour of the Np(V) solution vanished as the pH increased, this was attributed to the formation of (known [84VAR/HOB] [89RIG]) mixed hydroxo-carbonate Np(V) complexes. Before the end of the electrolysis, the solution could turn grey as already observed [84VAR/HOB], and Delmau found, that it was in fact due to a black precipitate. All these valuable observations are consistent with the interpretations given in this appendix: it explains the difficulties in preparing Np(IV) carbonate solutions [84VAR/HOB] [93LI/KAT], keeping it stable [79FED/PER], and the possibility of initial increase of pH [81WES/SUL].

The redox potential of a Np(V)/Np(IV) mixture was measured as in [79FED/PER]; but Delmau used a Pt electrode, and really succeeded to stabilise the potential for up to a week. Unfortunately she had not enough time to check some important measurements (pH, spectrophotometric determination of the [Np(V)]/[Np(IV)] ratio). Nevertheless, the redox potential and the formation constant, that she proposes, might well be more accurate than [79FED/PER] published ones (as estimated in this appendix). Both results are consistent. REVIEW OF THESE NUMBERS IS NOT FINISHED. For the equilibrium

$$Np(CO_3)_5^{6-} \Leftrightarrow NpO_2(CO_3)_3^{5-} + 2\ CO_2 + e^-$$

she proposes $E°' = 0.41$ or 0.51 V, $\Delta\varepsilon = -0.037$ or -0.032 kg/mol. then $\log_{10}\beta_5^{(IV)°} = 38\pm2$ and 41.06 at I=3M. My FIRST REINTERPRETATION is $E°'(P_{CO_2})=0.519$ V, $\Delta\varepsilon=-0.168$ kg/mol; assuming (as in [79FED/PER]), that the P_{CO_2} of the measurements were constant, if they had been equilibrated with the air $E°(1atm)=0.105$ V.

REVIEW OF T INFLUENCE. MORE DISCUSSIONS OF THE SPECTRA, AS FOR Pu, WE HAVE NOW SPECTRA IN A WIDE RANGE OF $[CO_3^{2-}]$ THAT SEEMS TO EXCLUDE THE EXISTENCE OF 3 COMPLEXES, TO BE COMPARED WITH (Ce or Th)$(CO_3)_i^{-2i+4}$ i=4, 5 AND 6 PROPOSED IN [73DERV/FAU-1 TO 3]; BUT WITH POSSIBLE INCONSISTENCY.

The dissociation constant of the Np(IV) limiting complex was determined by using a spectrophotometric technique as in [92CAP]; but the glass electrode is here calibrated with known buffers that reproduced most of the experimental conditions (CO_2 bubbling in Na_2CO_3 solution). Here again we would have liked to be able to perform some checking. Still, the U-Np-Pu analogy used in this appendix is confirmed. For the equilibrium

$$Np(CO_3)_5^{6-} \Leftrightarrow Np(CO_3)_4^{4-} + CO_3^{2-}$$

she proposes $\log_{10}K_5$=1.47, 1.63, 1.80, 1.79, 2.21and -0.98 ± 0.20 in 0.2, 0.3, 0.8, 1, 1.2 Na_2CO_3 solutions and extrapolated to I=0 by using the SIT, $\Delta\varepsilon=0.44$ kg/mol. FIRST REVIEW by Hélène Capdevila gives $\log_{10}K_5°=-1.35$, $\Delta\varepsilon=-0.06$ kg/mol.

2.16. [95VIT]

Vitorge P. *Neptunium en solution carbonate concentrée réductrice : bibliographie pour l'OCDE-AEN-TDB.* Note bibliographique CEA à paraître. (1995 vraisemblablement).

This is an early version of a part (appendix A on Np(IV) carbonate) of the present review, with supplementary materials.

3. Annexe: other references.

3.1. [58GEL/ZAI1]

Gel'man A.D., Zaitsev L. M. *Carbonate and oxalatocarbonate complex compounds of plutonium(IV). 1. Potassium Carbonatoplutonate.* Zhurn. Neorgan. Khimii., III, 6 (1958) 1304-1311, in Russian; Engl. transl.: J. Inorg. Chem. USSR III, 6 (1958) 47-58.

Solids are prepared, the following formulae are proposed $K_{2n-4}Pu(CO_3)_n.xH_2O$ with n = 4, 5, 6 and 8. "Certain proofs of the formation of a carbonate complex come from the solubility of Pu(IV) compounds in concentrated carbonate solutions (34-45 % K_2CO_3)". These proofs might be in "The actinide elements" by Seaborg and Katz together with some spectra by Fries and others. $(NH_4)_6Pu(CO_3)_5$ were precipitated out "when a green carbonate solution [certainly a concentrated $(NH_4)_2CO_3$ aqueous solution] of Pu(IV) is poured into 95 % ethyl alcohol" in an earlier (not published ?) work by Gel'man. "the hydroxide of Pu(IV) dissolves in concentrated carbonate solutions". Green solutions are formed in this reaction. The Pu(IV) carbonate solids are prepared from the Pu(IV) oxalate that "was dissolved in potassium, sodium or ammonium carbonate [aqueous solution]". This solution "was [then] poured into alcohol, upon which a green precipitate [...] fell out." The stoichiometries of these solid Pu(IV) carbonates were determined from chemical analysis, and the authors tried to check, whether they got single phases (not mixtures of solids and by products): X-ray analysis "showed that these products are not crystalline - they are amorphous". They could only obtain crystalline $K_6Pu(CO_3)_5$. For this, they let an aqueous solution ("without pouring it into alcohol") "to natural evaporation in the air at room temperature." This confirms or reveals the properties of Pu(IV), and probably of its chemical analogues: see the discussion on [71MOS5] in this review.

3.2. [58GEL/ZAI2]

Gel'man A.D., Zaitsev L. M. *2 Carbonatoplutonate of sodium.* Zhurn. Neorgan. Khimii., III, 7 (1958) 1551-1554, in Russian; Engl. transl.: J. Inorg. Chem. USSR III, 7 (1958) 102-106.

Solids are prepared, the following formulae are proposed: $Na_{2n-4}Pu(CO_3)_n.xH_2O$ with n = 4 and 5. Crystalline compounds are obtained.

3.3. [58MOS/GEL]

Moskvin, A.I., Gelman, A.D. *Determination of the composition and instability constants of oxalate and carbonate complexes of plutonium(IV)*, Russ. J. Inorg. Chem. 3, 4 (1958) 198-216.

3.4. [59GEL/ZAI]

Gel'man A.D., Zaitsev L. M. *Simple and complex plutonium(IV) Carbonates.* Zhurn. Neorgan. Khimii., 4, 12 (1959) 2688, in Russian; Engl. transl.: Russ. j. Inorg. Chem. IV, 12 (1959) 1243-1246.

Solids are prepared, the following formulae are proposed: $(NH_4)_{2n-4}Pu(CO_3)_n.xH_2O$ with n = 4, 5, 6.

3.5. [61GEL/MOS]

Gorbenko-Germanov D.S., Zenkova R.A. *Physical problems in spectroscopy.* In Russian, Izd. AN SSSR, Moscow 1 (1962) 422.

I have not this reference. It is reference [11] of [73KHA/MOS] 4029

3.6. [63RYA/VOL]

Ryabchikov D.I., Volynets M.P., Zarinskii V.A., Ivanov V.I. *High frequency titration Communication 7. A study of the carbonate compounds of thorium.* J. anal. chem. USSR 18 (1963) 307-313.

Reinterpretation could be tried ?

3.7. [69KHA/MOL]

Kharitonov Yu. Ya;, Molodkin A. K., Balakaeva T. A. *Infrared spectroscopic study of various carbonato-complexes of thorium.* Russ. j. Inorg. Chem. 14, 10 (1969) 1453-1456.

Monodentate and bidentate carbonate ligands.

3.8. [70UEN/HOS]

Ueno K. Hoshi M. *The precipitation of some actinide element complex ions by using hexammine cobalt(III) cation, I.: The precipitation of thorium and plutonium(IV) carbonate complex ions with hexammine cobalt(III) chloride*, J. Inorg. Nucl. Chem., 39 (197) 315-318.

3.9. [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.

3.10. [72DER]

Dervin J *Sur la structure et la stabilité des carbonates complexes de thorium(IV), cérium(IV), zirconium(IV), hafnium(IV)*. Thèse, Université de Reims France (1973).

The formation constants of $M(CO_3)_4^{4-}$, $M(CO_3)_5^{6-}$ and $M(CO_3)_6^{8-}$ (M = Ce or Th) are measured by several methods; but there is no attempt to check the possible formation of mixed hydroxo-carbonate or polynuclear complexes, and it is not sure that the relative stability of these complexes are consistent in all the media used by the author (this should be calculated). This work gives much useful experimental information, reinterpreting should then be worthwhile. For this, $[CO_3^{2-}]$ should first be recalculated (it is not always very clear how the author determined it their experimental conditions), activity corrections should be improved, and the proposed (or recalculated) formation constant values should then be compared to all the experiments (they do not seem to be always consistent).

3.11. [73DER/FAU1]

Dervin J., Faucherre J. Herpin P., Voliotis S. n°473 - *Etude de la solubilité des carbonates complexes de thorium et de cérium. I. - Domaines d'existence, préparation et données cristallographiques des composés solides.* Bull. soc. chim. France 9-10 (1973) 2634-2637. Part of [72DER].

3.12. [73DER/FAU2]

Dervin J., Faucherre J. n°542 - *Etude de la solubilité des carbonates complexes de thorium et de cérium. II.- Constitution des complexes en solution*. Bull. soc. chim. France 11 (1973) 2926-2929. Part of [72DER].

3.13. [73DER/FAU3]

Dervin J., Faucherre J. n°543 - *Etude de la solubilité des carbonates complexes de thorium et de cérium. III.- Solubilité et nature des ions complexes en solution.* Bull. soc. chim. France 11 (1973) 2930-2933. Part of [72DER].

$Na_6An(CO_3)_5.12H_2O$ (An = Ce or Th) solubility, S, in concentrated Na_2CO_3 and $NaHCO_3$ solutions, is practically constant in a wide range of $[CO_3^{2-}]$: S = 0.0215 and 0.015 M respectively for thorium and cerium. $[Na^+]$ was maintain constant (with a sodium salt ?) at 2 g/l. The authors assume, that CO_3^{2-} is the only ligand of the soluble complexes; but they do not discuss this assumption. Since the solubility is the same in the Na_2CO_3 and $NaHCO_3$ solutions of similar $[CO_3^{2-}]$, $[Na^+]$ and activity of water, this confirms the author assumption. This could demonstrate, that $An(CO_3)_5^{6-}$ is the major species; but the ionic strength corrections are not as straightforward as done by the authors, who might as well have seen some ion pairing between Na^+ and the anionic soluble carbonate complex. Anyhow, I do not check these interpretations.

3.14. [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.

3.15. [75VOL]

Voliotis S. *Etude structurale des carbonates complexes de cérium et de thorium.* Thèse de doctorat es sciences, université Paris VII, France (1975).

3.16. [75VOL/RIM1]

Voliotis S., Rimsky A., Faucherre J. *Etude structurale des carbonates complexes de cérium et thorium. I. Structure cristalline et moléculaire du pentacarbonatocérate de guanidine tétraahydraté,* $[C(NH_2)_3]_6[Ce(CO_3)_5].4H_2O$. Acta Cryst. B31 (1975) 2607-2611.

3.17. [75VOL/RIM2]

Voliotis S., Rimsky A., *Etude structurale des carbonates complexes de cérium et thorium. II. Structure cristalline et moléculaire du pentacarbonatothorate de guanidine tétraahydraté,* $[C(NH_2)_3]_6[Th(CO_3)_5].4H_2O$. Acta Cryst. B31 (1975) 261-2615.

3.18. [75VOL/RIM3]

Voliotis S., Rimsky A. *Etude structurale des carbonates complexes de cérium et thorium. IV. Structure cristalline et moléculaire du pentacarbonatothorate de sodium dodécahydraté,* $Na_6[Th(CO_3)_5].12H_2O$. Acta Cryst. B31 (1975) 2615-2620.

3.19. [75VOL/RIM4]

Voliotis S., Rimsky A. *Etude structurale des carbonates complexes de cérium et thorium. IV. Structure cristalline et moléculaire du pentacarbonatocérate de sodium dodécahydraté,* $Na_6[Ce(CO_3)_5].12H_2O$. Acta Cryst. B31 (1975) 2620-2622.

3.20. [77VOL/FRO]

Voliotis S., Fromage F., Faucherre J., Dervin J., . *Corrélations structures-propriétés chez les pentacarbonates complexes de thorium et de cérium.* Revue Chim. Min.. 14, 5 (1975) 441-446.

3.21. [80JOL/THO]

Jolivet J.P., Thomas Y., Taravel B., Lorenzelli V. *Vibrational study of coordinates* $CO_3^{=}$ *ions*. J. Molecular Struct. 60 (1980) 93-98.

3.22. [80PAK/KHE]

Pakholkov V. S., Khe S. D., Markov V. F. *Separation of uranium and thorium in solutions of ammonium carbonate with granulated ferric hydroxide.* Soviet Radiochem. 22, 1 (1980) 23-26 transl. from Radiokhim. 22, 1 (1980) 38-42.

Reinterpretation could be tried?

3.23. [82JOL/THO]

Jolivet J.P., Thomas Y., Taravel B., Lorenzelli V. Busca G. *Infrared determination of the coordination state of* $CO_3^{=}$ *ions* in *cerium and thorium tetracarbonnato complexes*. J. Molecular Struct. 79 (1982) 403-408.

3.24. [83JOL/THO]

Jolivet J.P., Thomas Y., Taravel B., Lorenzelli V. Busca G. *Infrared spectra of cerium and thorium pentacarbonnate complexes*. J. Molecular Struct. 79 (1982) 403-408.

3.25. [83KIM/LIE]

Kim J. I., Lierse C. H., Baumgartner F. ACS Symp. 216 (1983) 318.

3.26. [87JOA/BIG]

Etude des carbonates complexes des éléments IVB I - détermination de la constante de stabilité du pentacarbonatothorate (IV). Bul. soc. chim. France 1 (1987) 42-44.

Reinterpretation could be tried.

3.27. [88MAR/HER]

Marsh R. E., Herbstein F.H. *Structure of* $Guanidine_6Th(CO_3)_5$, Acta Cryst. B44 (1988) 77.

3.28. [88NAG/TAN]

Nagasaki, S., Tanaka, S., Takahashi, Y. *Speciation and solubility of neptunium in underground environments by paper electrophoresis*, J. Radioanal. Nucl. Chem., 124 (1988) 383-395.

3.29. [89RIG]

Riglet, C. *Chimie du neptunium et autres actinides en milieu carbonate, Thèse, Université Paris 6* 1989. 267p, in French, see [90RIG].

3.30. [89RIG/ROB]

Riglet, C., Robouch, P., Vitorge, P. *Standard potentials of the* (MO_2^{+2}/MO_2^{+}) *and* (M^{+4}/M^{+3}) *redox systems for neptunium and plutonium*, Radiochim. Acta, 46 (1989) 85-94.

3.31. [90HAL/FOU]

Haltier E., Fourest B., David F. *Spectroelectrochemical study of uranium and cerium in carbonate media.* Radiochim. Acta 51 (1990) 107-112.

Reinterpretation could be tried.

3.32. [90RIG]

CEA-R-5535 (1990). Commissariat a l'Energie Atomique, Gif-sur-Yvette, France. It is [89RIG].

3.33. [90YAM/PUS]

Yamnova N.A., Pushcharovskii D.Y., Voloshin A.V. $Na_6BaTh(CO_3)_6.H_2O$ *structure.* Sov. Phys. Dokl., 35 (1990) 12.

3.34. [91VIT]

Vitorge P. *Solubility limits of radionuclides in interstitial water. Americium in cement.* EUR 13664.

3.35. [92CAP]

Capdevila H. *Données thermodynamiques sur l'oxydoréduction du plutonium en milieux acide et carbonate. Stabilité de Pu(V)* Thèse Paris-sud (Paris 11) Université Orsay centre (5 June 1992). See [93CAP].

3.36. [92GRE/FUG]

Grenthe, I., Fuger, J., Konings, R.J.M., Lemire, R.J., Muller, A.B., Nguyen-Trung, C., Wanner, H. *Chemical thermodynamics of uranium* (Wanner, H., Forest, I., eds.), Amsterdam: Elsevier Science Publishers B.V., 1992, 715p.

3.37. [93CAP]

CEA-R-5643 (1993). Commissariat a l'Energie Atomique, Gif-sur-Yvette, France. It is [92CAP].

3.38. [95CAP/VIT]

Capdevila H., Vitorge P., Delmau L. H., *Spectrophotometric study of the stability of Pu(IV) and Np(IV) limiting carbonate complexes,* to be presented at Migration 1995 (Saint-Malo, France).

3.39. [95SIL/BID]

Silva R. J., Bidoglio G., Rand M.H., Robouch P. B., Wanner H., Puigdomenech I., edited by Puigdomenech I., *Chemical thermodynamics of americium* TDB-AEN-OECD and ed. to be published in 1995.

4. Published experimental data (or to be published)

We tabulate the values, that we have taken (usually scanned) from the publications. The definitions written at the top of some tables are usually the same for all the tables.

4.1. [71MOS5]

c = $[(NH_4)_2CO_3]$ (mole/l), lg = $\log_{10}$ s4, 5 or 6 = Np(IV, V or VI) solubilité (mole/l), Np(ini) = forme chimique sous laquelle est introduite le neptunium.

Np(ini)		Np^{4+}			$NH_4NpO_2CO_{3s}$			NpO_2^+		
c	lgc	s4	pH	lgs4	S5	pH	lgS5	s5	pH	lgs5
0.00		6.17E-03	8.60	-2.21	1.00E-05	8.80	-5.00	7.94E-06	8.60	-5.10
0.10	-1.00									
0.15	-0.82	6.92E-03	8.60	-2.16						
0.20	-0.70				1.51E-05	8.80	-4.82	1.17E-05	8.60	-4.93
0.25	-0.60									
0.30	-0.52									
0.45	-0.35									
0.50	-0.30							1.69E-05	8.60	-4.77
0.60	-0.22	8.91E-03	8.65	-2.05	4.51E-05	8.80	-4.35			
0.75	-0.12							5.51E-05	8.70	-4.26
1.00	0.00	1.32E-02	8.70	-1.88	6.20E-05	8.90	-4.21	8.70E-05	8.75	-4.06
1.25	0.10				1.00E-04	8.90	-4.00	1.78E-04	8.80	-3.75
1.50	0.18	1.74E-02	8.70	-1.76	1.23E-04	9.00	-3.91	2.66E-04	8.80	-3.58
1.80	0.26	1.90E-02	8.75	-1.72				3.55E-04	8.85	-3.45
2.00	0.30				1.05E-04	9.00	-3.98	2.29E-04	8.90	-3.64
2.20	0.34	2.19E-02	8.80	-1.66	7.81E-05	9.00	-4.11	1.06E-04	9.00	-3.97

Np(ini)		NpO_2OH_s			$(NH_4)_2Np\ O_2(CO_3\ )_{3s}$		
c	lgc	s6	pH	lgs6	S6	pH	lgS6
0.00		7.94E-04	8.80	-3.10	1.06E-01	8.50	-0.97
0.10	-1.00	3.29E-03	8.80	-2.48	6.54E-02	8.55	-1.18
0.15	-0.82	6.67E-03	8.82	-2.18			
0.20	-0.70	1.44E-02	8.85	-1.84			
0.25	-0.60	1.84E-02	8.90	-1.74			
0.30	-0.52	1.93E-02	8.95	-1.71			
0.45	-0.35	2.14E-02	9.00	-1.67			
0.50	-0.30				2.26E-02	8.60	-1.65
0.60	-0.22	2.12E-02	9.05	-1.67			
0.75	-0.12	1.56E-02	9.07	-1.81	1.60E-02	8.70	-1.80
1.00	0.00	1.33E-02	9.10	-1.88	1.27E-02	8.80	-1.90
1.25	0.10	8.23E-03	9.10	-2.08	8.86E-03	8.90	-2.05
1.50	0.18				8.31E-03	8.95	-2.08
1.80	0.26				6.65E-02	9.05	-1.18
2.00	0.30						
2.20	0.34				4.51E-03	9.10	-2.35

4.2. [77UEN/SAI]

C = $[(NH_4)_2CO_3]$, C1 = $[Co(NH_3)_6Cl_3]$, S and [Np(IV] are Np(IV) solubility.

C	C1	S(g/l)	lgS(g/l)	lg C	lg C1	lg[Np(IV)]
0.103	0.04	0.0007	-3.154	-0.987	-1.398	-5.529
0.305	0.04	0.0013	-2.883	-0.516	-1.398	-5.257
0.504	0.04	0.0026	-2.583	-0.298	-1.398	-4.958
0.703	0.04	0.0068	-2.171	-0.153	-1.398	-4.545
0.897	0.04	0.0027	-2.57	-0.047	-1.398	-4.945
0.3	0.0983	0.0006	-3.225	-0.523	-1.007	-5.6
0.3	0.3	0.0009	-3.05	-0.523	-0.523	-5.425
0.3	0.502	0.0014	-2.854	-0.523	-0.299	-5.229
0.3	0.701	0.0016	-2.8	-0.523	-0.154	-5.175
0.3	0.9	0.0017	-2.775	-0.523	-0.046	-5.15

4.3. [85RAI/RYA]

Ke = $[OH^-]\, a_{H^+} / a_{H_2O}$, a_X is X activity (mol/kg), [X] is X concentration (mole/l), X is also X concentration (mole/kg), a1 = $lg(a_{CO_3^{2-}}) - lg(a_{OH^-})$, [1] = $lg[CO_3^{2-}] - lg[OH^-]$, M is the total carbonate concentration (mole/l), a4/5 = $lg(a_{CO_3^{2-}}) - 4lg(a_{OH^-})/5$, a4/3 = $lg(a_{CO_3^{2-}}) - 4lg(a_{OH^-})/3$, lg is log_{10}, in the tables the charge are omitted, no indice are used.

pH	lg[NpIV]	lgKe	$lg[OH^-]$	$lg[CO_3^{2-}]$	$lg(a_{OH^-})$	$lg(a_{CO_3^{2-}})$	a1	[1]	lg M	a4/5	a4/3
mesure	mesure	-13.956	-5.713	-3.962	-5.757	-4.141	1.616	1.7506	-2		
8.9	-8.15	-13.955	-5.055	-3.314	-5.100	-3.499	1.602	1.7409	-2	0.581	3.302
10.1	-8.45	-13.942	-3.842	-2.328	-3.900	-2.564	1.336	1.5142	-2	0.556	2.636
10.4	-8.35	-13.938	-3.538	-2.190	-3.600	-2.444	1.157	1.3481	-2	0.437	2.357
11	-8.45	-13.933	-2.933	-2.054	-3.000	-2.331	0.670	0.8786	-2	0.069	1.670
11.9	-8	-13.924	-2.024	-2.007	-2.100	-2.319	-0.219	0.0176	-2	-0.639	0.481
12.15	-8.4	-13.919	-1.769	-2.004	-1.850	-2.339	-0.488	-0.234	-2	-0.858	0.129
12.9	-7.7	-13.888	-0.988	-2.001	-1.102	-2.489	-1.387	-1.013	-2	-1.607	-1.020
13.5	-8.4	-13.857	-0.357	-2.000	-0.506	-2.720	-2.214	-1.643	-2	-2.315	-2.045
13.8	-8.4	-13.857	-0.057	-2.000	-0.212	-2.861	-2.649	-1.943	-2	-2.691	-2.578

4.4. [89MOR/PRA]

lgS	pH	$lg[OH^-]$	$lg[CO_3^{2-}]$	lg M	$lg(a_{OH^-})$	$lg(a_{CO_3^{2-}})$	[4/5]	[1]	[4/3]	a1	a4/5
-4.780	9.100	-4.775	-2.834	-2.010	-4.909	-3.463	0.987	1.942	3.533	1.446	0.464
-5.450	8.950	-4.925	-3.134	-2.179	-5.059	-3.763	0.807	1.792	3.433	1.296	0.284
-4.760	8.900	-4.975	-3.234	-2.234	-5.109	-3.863	0.747	1.742	3.400	1.246	0.224
-5.200	8.900	-4.975	-3.234	-2.234	-5.109	-3.863	0.747	1.742	3.400	1.246	0.224
-6.060	8.800	-5.075	-3.434	-2.343	-5.209	-4.063	0.627	1.642	3.333	1.146	0.104
-5.360	8.800	-5.075	-3.434	-2.343	-5.209	-4.063	0.627	1.642	3.333	1.146	0.104
-5.740	8.600	-5.275	-3.834	-2.555	-5.409	-4.463	0.387	1.442	3.200	0.946	-0.136
-5.830	8.600	-5.275	-3.834	-2.555	-5.409	-4.463	0.387	1.442	3.200	0.946	-0.136
-6.230	8.350	-5.525	-4.334	-2.814	-5.659	-4.963	0.087	1.192	3.033	0.696	-0.436
-5.830	8.300	-5.575	-4.434	-2.865	-5.709	-5.063	0.027	1.142	3.000	0.646	-0.496

4.5. [90PRA/MOR]

lgS	pH	lg[OH^-]	lg[CO_3^{2-}]	lg M	lg(a_{OH^-})	lg($a_{CO_3^{2-}}$)	[4/5]	[1]	[4/3]	a1	a4/5
-7.200	8.050	-5.906	-4.156	-2.000	-5.950	-4.336	0.568	1.750	3.718	1.614	0.424
-6.290	8.200	-5.756	-4.006	-2.000	-5.800	-4.186	0.598	1.750	3.668	1.614	0.454
-6.400	8.500	-5.456	-3.706	-2.000	-5.500	-3.886	0.659	1.750	3.569	1.614	0.514
-6.400	8.700	-5.256	-3.509	-2.000	-5.300	-3.691	0.696	1.747	3.499	1.609	0.549
-5.920	8.600	-5.356	-3.607	-2.000	-5.400	-3.788	0.677	1.749	3.534	1.612	0.532
-6.680	9.200	-4.753	-3.029	-2.000	-4.800	-3.221	0.773	1.724	3.308	1.579	0.619
-6.710	9.650	-4.299	-2.637	-2.000	-4.350	-2.846	0.802	1.662	3.095	1.504	0.634
-6.410	9.700	-4.248	-2.597	-2.000	-4.300	-2.810	0.801	1.651	3.067	1.491	0.631
-6.500	9.850	-4.096	-2.486	-2.000	-4.150	-2.707	0.791	1.610	2.975	1.443	0.613
-6.880	10.200	-3.741	-2.276	-2.000	-3.800	-2.518	0.717	1.465	2.712	1.282	0.522
-6.140	10.000	-3.944	-2.387	-2.000	-4.000	-2.617	0.768	1.557	2.872	1.383	0.583
-5.900	10.000	-3.944	-2.387	-2.000	-4.000	-2.617	0.768	1.557	2.872	1.383	0.583
-5.650	9.700	-4.248	-2.597	-2.000	-4.300	-2.810	0.801	1.651	3.067	1.491	0.631
-5.790	10.400	-3.538	-2.190	-2.000	-3.600	-2.444	0.640	1.348	2.527	1.157	0.437
-6.210	10.500	-3.437	-2.156	-2.000	-3.500	-2.415	0.593	1.281	2.427	1.086	0.386
-6.200	10.600	-3.336	-2.127	-2.000	-3.400	-2.390	0.541	1.209	2.320	1.010	0.330
-6.340	10.600	-3.336	-2.127	-2.000	-3.400	-2.390	0.541	1.209	2.320	1.010	0.330
-6.700	10.600	-3.336	-2.127	-2.000	-3.400	-2.390	0.541	1.209	2.320	1.010	0.330
-6.700	11.000	-2.933	-2.054	-2.000	-3.000	-2.331	0.292	0.879	1.856	0.669	0.069
-6.590	11.000	-2.933	-2.054	-2.000	-3.000	-2.331	0.292	0.879	1.856	0.669	0.069
-6.490	11.100	-2.832	-2.043	-2.000	-2.900	-2.323	0.222	0.789	1.733	0.577	-0.003
-6.620	12.000	-1.923	-2.005	-2.000	-2.001	-2.326	-0.467	-0.083	0.558	-0.325	-0.725
-6.410	11.800	-2.126	-2.009	-2.000	-2.200	-2.315	-0.308	0.117	0.826	-0.114	-0.554
-6.410	12.200	-1.718	-2.003	-2.000	-1.801	-2.344	-0.629	-0.285	0.288	-0.544	-0.904
-6.500	11.900	-2.024	-2.007	-2.000	-2.101	-2.319	-0.387	0.018	0.692	-0.219	-0.639
-6.520	12.200	-1.718	-2.003	-2.000	-1.801	-2.344	-0.629	-0.285	0.288	-0.544	-0.904

4.6. [95DEL]

Laætitia Delmau, rapport de DEA à paraître en CEA-Note (1995)

Table [95DEL]-1 Laætitia Delmau's spectrophotometric results Spectrophotometric measurements in Na_2CO_3 solutions, where CO_2 gas is bubbled, are interpreted (over 3 pH units), with the equilibrium $Np(CO_3)_4^{4-} + CO_3^{2-} \leftrightarrow Np(CO_3)_5^{6-}$. The equilibrium constant, K_5 (M^{-1}), is measured at the half point reaction, at 1013, 990 and 823 nm. *curve fitting by Hélène Capdevila from the same experimental data, in this case, uncertainty is 1.5 standard deviation.

$\varepsilon_{Np(CO_3)_4^{4-}}$ ($cm^{-1}M^{-1}$)	$\varepsilon_{Np(CO_3)_5^{6-}}$ ($cm^{-1}M^{-1}$)	$[Np]_t$ (mM)	2.82	2.82	2.82	2.82	3.40	(SIT regression)	
		$[Na_2CO_3]$ (M)	0.2	0.3	0.4	0.5	0.6	0	*0
8.53±0.9	28.9±2.9	$\log_{10}K_5$ at 1013 nm	1.39	1.69	1.85	1.92	2.19		
40.6±4.1	8.44±0.9	990 nm	1.45	1.64	1.76	1.66	2.20		
54.5±5.5	20.5±2.1	823 nm	1.58	1.57	1.79	1.79	2.25		
		mean of $\log_{10}K_5$	1.47	1.63	1.80	1.79	2.21	-0.98	-1.35*
		uncertainty	0.08	0.05	0.04	0.10	0.03	0.20	0.17*
		Δε (mole/kg)						0.44	-0.06*
		uncertainty						0.05	0.36*

Table [95DEL]-2 Laætitia Delmau's redox results E is Np(V)/Np(IV) redox potential (mV/SHE), M = $[Na_2CO_3]$ (mole/l), m_{Na^+} is Na^+ concentration (mole/kg), D is the Debye-Hückel term [92GRE/FUG] see the text for our calculation of E'° and Y.

E	M	m_{Na^+}	D	lg P_{CO_2}	lg(a_{OH^-})	lg($a_{CO_3^{2-}}$)	E'°	Y
247	0.3	3.062	0.258	-3.5	-3.746	-1.084	0.661	8.328
234	0.6	2.029	0.245	-3.5	-3.767	-1.146	0.648	8.263
244	1	1.211	0.226	-3.5	-3.813	-1.252	0.658	8.642
228	1.5	0.603	0.197	-3.5	-3.894	-1.427	0.642	8.676

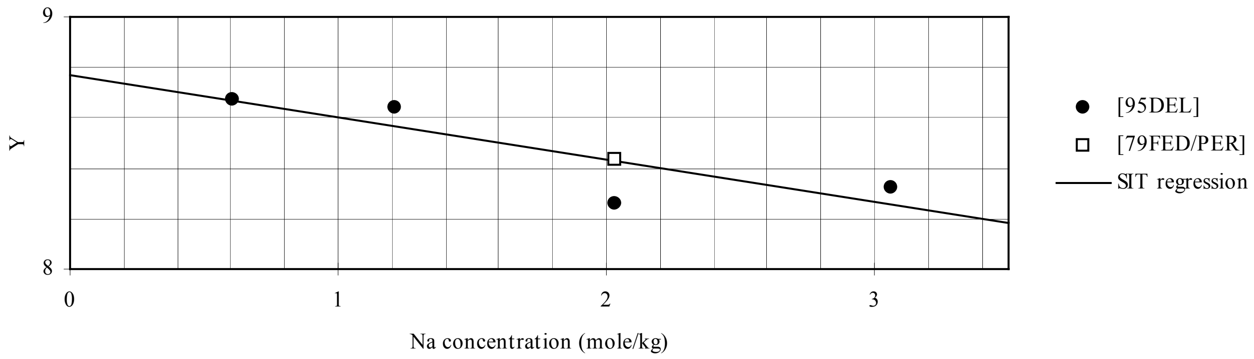


Figure [95DEL]-1: SIT regression on the redox potential of the Np(V)/Np(IV) couple in Na_2CO_3 media. The measured potential E_m, is corrected for P_{CO_2} assuming equilibration with the air E = E_m - 2 × 0.05916 $\log_{10}P_{CO_2}$. Y = E / 0.05916 - 11 D. [95DEL] is not yet published, its reviewing is not yet finished. The correction of E_m for the [Np(V)] / [Np(IV] ratio cannot be checked in [79FED/PER] and has not yet been checked in [95DEL]. The junction potential and the calibration of the reference electrode cannot be checked in [79FED/PER]; they seem to be correct in [95DEL]. SIT regression (m_{Na^+} , Y) gives Δε = -0.168; Y° = 8.767, then E'°(P_{CO_2} = $10^{-3.5}$ atm) = 0.519 V/SHE, is a formal potential in standard conditions except for P_{CO_2}. E'°(P_{CO_2} = 1 atm) = E'°(P_{CO_2} = $10^{-3.5}$ atm) - 7 × 0.05916 = 0.105 V/SHE. Equilibration with the air was not checked in these works. $\log_{10}P_{CO_2}$ could then be smaller than -3.5. This would lower E and then E'° by several orders of magnitude. The formation constant of the $Np(CO_3)_5^{6-}$ estimated from this type of measurement (see the discussion on [79FED/PER] in the Appendix A) would then be higher by several orders of magnitudes. This is "unbelievable" [85RAY/RIAN].

In the calculations we assume, that the carbonic gas partial pressure P_{CO_2} (atm) is equilibrated with the air. If the redox equilibrium is $Np(CO_3)_5^{6-} \leftrightarrow NpO_2(CO_3)_3^{5-} + 2\ CO_2 + e^-$, E'° = E(mV) / 1000 - 2 x 0.05916 lg P_{CO_2} (V/SHE). Y = E'° / 0.05916 - 11 D. SIT regression (m_{Na^+} , Y) gave Δε = -0.168; Y° = 8.767, then E° = 0.519 V/SHE. E'° = E°(P_{CO_2} = $10^{-3.5}$ atm) is a formal potential in standard conditions except for P_{CO_2}. E°(P_{CO_2} = 1 atm) = E'° - 7 x 0.05916 = 0.105 V/SHE. These values are used to plot the figure[95DEL]-1. REVIEWING OF THIS WORK IS NOT FINISHED, IT WILL BE IN APPENDIX A WHEN [95DEL] WILL BE PUBLISHED..

4.7. [95OFF/VIT]

Offerlé S., Vitorge P., Capdevila H. *Np(VI)/Np(V) en milieu carbonate concentré.* NOTE CEA-N-2785 (1995).

5. Projet du § VI.6.1.1.3 Np(IV) carbonate complexes

by Pierre Vitorge

Second draft of § VI.6.1.1.3, part of OECD NEA TDB Chemical Thermodynamics of Neptunium & Plutonium

VI Discussion of neptunium data selection

VI.6 Group 14 compounds and complexes

VI.6.1 Neptunium carbonates

VI.6.1.1 The aqueous neptunium-carbonate system

THERE ARE SOME GENERAL COMMENTS IN THE CORRESPONDING § OF THE U VOLUME. I SUGGEST TO REPEAT MOST OF THEM. WE COULD ADD FIGURES SHOWING SPECIATION IN M_2CO_3 (M = Na AND NH_4, MAYBE ALSO K) AND $NaHCO_3$ SOLUTIONS.

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. No precise thermodynamic data and quantitative interpretation can then be deduced from them. We still consider these data since there are too few other experimental results. In concentrated M_2CO_3 media, $\lg P_{CO_2}$ quickly vary from -7 or -6 to -3.5 (it is not buffered). This typically induces up to nearly seven orders of magnitude of formation constant deduced from redox measurements of the Np(V)/Np(IV) couple.

VI.6.1.1.1 Np(VI) carbonate complexes

I HOPE TO WRITE THE FIRST DRAFT BEFORE THE END OF THIS YEAR.

I SHOULD EASILY deduce the formation constant, β_3, of the limiting complex, $NpO_2(CO_3)_3^{4-}$, from redox measurements (see table). *A first estimate [92CCAP] is* $\log_{10}\beta_3 \approx 20.4 \pm 1.0$ *at I = 0, that is not far from the U value (21.60 ± 0.05) [92GRE/FUG].*

§ VI.6.1.1.1 OF THE DRAFT OF MAY 90 WILL THEN BECOME

VI.6.1.1.2 Major Np(V) carbonate complexes

I MUST DO SOME CORRECTIONS AND RECALCULATIONS ON THIS §, BUT THIS SHOULD NOT CHANGE MUCH THE NUMBERS OF THE SOLUBLE CARBONATE COMPLEXES OF Np(V).

VI.6.1.1.3 Np(IV) carbonate complexes

There is not any published work from which the stoichiometry of the limiting carbonate complex of Np(IV) can be deduced. Rai and Ryan (see the discussion on [85RAI/RYAN] and [71MOS5] in the Appendix A) pointed out, that the only work published before 1985 [71MOS5], that proposed the stoichiometry, and the formation constant of a Np(IV) carbonate complex, is "completely erroneous", "unbelievable". This revue agrees with Rai end Ryan comments (see appendix A and below). Unfortunately Moskvin's or other incorrect complexation constants are still being used [88NAG/TAN] [89MOR/PRA] [89PRA/MOR] [89TAN/NAG] [90PRA/MOR] [91ITA/TAN] [91PRA/YAM] [93PRA/YAM].

The stoichiometry and the stability of the limiting complex of U(IV) [83] [8] [92GRE/FUG] and Am(IV) [95SIL/BID] seem to be $M(CO_3)_5^{6-}$ (M = U and Am). $M(CO_3)_6^{8-}$ (now M = Th or Ce) has been proposed in concentrated carbonate aqueous solutions [72DER] [73DER/FAU2] [73DER/FAU3], and $Th(CO_3)_6^{8-}$ have been found in a solid compound [90YAM/PUS]; but this stoichiometry is not well established in aqueous solutions. $Am(CO_3)_6^{8-}$ does not exist, maybe only because its ionic radius is

Table VI.6.1.1.1-a : Redox potential of the Np(VI)/Np(V) couple in concentrated carbonate media.

reference	E (V/SHE)	method	T (°C)	I (M) and medium
[74SIM/VOL]	0.440±0.010	cou		0.2 to 3 M K_2CO_3
[75SIM]	0.460±0.020	cou		1 M Na_2CO_3, pH = 11.5
[81WES/SUL] and [85NEW/SUL]	0.445±0.010	vlt		1 M Na_2CO_3
[95OFF/VIT]	0.504±0.010		25	1 M Na_2CO_3
[84VAR/HOB]	0.454±0.010	vlt		2 M Na_2CO_3
[95OFF/VIT]	0.517±0.010		25	2 M Na_2CO_3
[89RIG]	0.496±0.030	vlt		0.1 M HCO_3^-, 3 M Na^+, ClO_4^-

Table VI.6.1.1.3-b : Published values of the temperature influence on the redox potential of the Np(VI)/Np(V) couple in Na_2CO_3 solutions. There is only one publication [95OFF/VIT], it uses cyclic voltammetry

E	±	ΔS	ΔCp	T	[Na_2CO_3]	E	±	ΔS	ΔCp	T	[Na_2CO_3]
(V/SHE)		(mV/K)	($J.K^{-2}mol^{-1}$)	(°C)	(M)	(V/SHE)		(mV/K)	($J.K^{-2}mol^{-1}$)	(°C)	(M)
0.465				5	0.22	0.543_5				5	1.25
0.455_5				15		0.527				15	
0.436	0.008	-159	-463	25		0.502	0.012	-200	180	25	
0.418				35		0.475_5				35	
0.401				45		0.458_5				45	
0.381_5				55		0.451				55	
						0.441				60	
0.501_5				5	0.55	0.544_7				5	1.5
0.484				15		0.527_5				15	
0.469	0.008	-164	-246	25		0.504	0.010	-197	355	25	
0.452_5				35		0.485				35	
0.432_5				45		0.462				45	
0.411_5				55		0.444_3				55	
						0.437				60	
0.537				5	1	0.568				5	2 M
0.520				15		0.548_5				15	
0.504	0.010	-169	29	25		0.517	0.010	-230	652	25	
0.487_5				35		0.492_5				35	
0.465				45		0.475_3				45	
0.447				55		0.459_5				55	
0.437				60		0.448_5				60	

Table VI.6.1.1.1-c : Published values of the temperature influence on the redox potential of the Np(VI)/Np(V) couple extrapolated to zero ionic strength in Na_2CO_3 solutions. There is only one publication **[95OFF/VIT]** with measurements at several T, the data are extrapolated [95OFF/VIT] from the data of the Table VI.6.1.1.1-c.

E	ΔS°	ΔCp°	Δε	Δε'	Δε"	T
(V/SHE)	(J/K/mol)	($J.K^{-2}mol^{-1}$)	kg/mol	kg/mol/K	kg/mol/K^2	(°C)
0.375			0.29_6			5
0.358			0.23_8			15
0.341±0.014			0.15_5±0.04	-0.005_1±0.001	0.00004_0	25
0.336*±0.014	-190*±45	345*±750	0.17_8*			25*
0.319			0.11_3			35
0.294			0.10_0			45
0.269			0.10_6			55
0.285			-0.03_0			60

smaller than the U one, and $U(CO_3)_6^{8-}$ have not been seen maybe only because [CO_3^{2-}] was not high enough: these two hypotheses cannot be rejected from experimental data, but we do not believe them. Anyhow (see below), the extensive spectrophotometric studies on Np(IV) in carbonate media ([71MOS5] [77SAI/UEN] [81WES/SUL] [84VAR/HOB] [93LIT/KAT] and specially [95DEL]) indicate, that the carbonate limiting complex of Np(IV) is stable in quite a wide range of chemical conditions, where $Np(CO_3)_6^{8-}$ formation seems to be quite unbelievable. All the published work on lanthanide and actinide(IV) in concentrated carbonate aqueous solutions or in carbonate solids can be interpreted as confirmation of the analogous behaviour of the f element series. To test this hypothesis , we shall then first assume, that the limiting complex of Np(IV) is $Np(CO_3)_5^{6-}$. The dissociated one is then $Np(CO_3)_4^{4-}$ (see below).

5.1. Spectrophotometric measurements.

The first experimental evidence of carbonate complexation of neptunium is the absorption spectrum of Np(IV) in carbonate media [71MOS5], that been confirmed later [77SAI/UEN] [81WES/SUL] [84VAR/HOB] [93LIT/KAT] [95DEL]. These spectra clearly show, that the limiting complex of Np(IV) is stable in Na_2CO_3 solutions of concentration more than 0.3 M. *(IN 1 M $NaHCO_3$ ONES, SEE THE DISCUSSION OF [81WES/SUL] AND [95DEL] IN THE APPENDIX A: IT IS NOT YET CLEAR WHETHER THE EXPERIMENTAL RESULTS OF THESE 2 STUDIES, ARE CONSISTENT, IS NOT YET [95DEL] REVIEWED)*. This behaviour is similar to the U [92GRE/FUG] and Pu (§ ?) one. It is consistent with Ray and Ryan [85RAY/RYA] solubility measurement (see also the discussion on [71MOS5] and [79FED/PER] in the Appendix A).

The limiting complex is dissociated when decreasing the ionic strength or the free carbonate concentration (see [95DEL] and the discussion on [93LI/KAT] -AND [77SAI/UEN] TO BE IMPROVED- in the Appendix A). One carbonate ion and no hydroxide ion is exchanged between the limiting and the dissociated complex [95DEL]. This occurs in similar conditions as U [92GRE/FUG] and Pu [92CAP]. The constant, K_5, of the equilibrium

$$M(CO_3)_4^{4-} + CO_3^{2-} <==> M(CO_3)_5^{6-}$$

is $\log_{10}K_5$ = *-1.35 ± 0.17* (*FIRST RECALCULATION FROM [95DEL] DATA*), $\varepsilon(Np(CO_3)_5^{6-}, Na^+) - \varepsilon(Np(CO_3)_4^{4-}, Na^+) - \varepsilon(CO_3^{2-}, Na^+)$ = *-0.06 ± 0.36 kg/mol.* (*FIRST RECALCULATION FROM [95DEL] DATA*). Assuming that $\varepsilon(Np(CO_3)_4^{4-}, Na^+) \approx \varepsilon(U(CO_3)_4^{4-}, Na^+) = 0.09 \pm 0.10$ kg/mole [92GRE/FUG], $\varepsilon(Np(CO_3)_5^{6-}, Na^+) \approx$ *0.08 ± 0.5 kg/mol. NOT IN AGREEMENT WITH THE ESTIMATION (BLOW) FROM REDOX MEASUREMENTS, THESE NUMBERS SHOULD BE CHANGED, WHEN REVIEWING [95DEL], AND* K_5 *VALUES SHOULD BE RECALCULATED FROM [77SAI/UEN] AND [93LI/KAT] (AT LEAST) DATA.*.

5.2. Measurement of the redox potential of the Np(V)/Np(IV) couple.

Since the limiting complex of Np(V) (§VI.6.1.1.2), and the standard potential of the NpO_2^+/Np^{4+} redox couple are well known; studying the Np(V)/Np(IV) redox couple could give useful information on the stoichiometry of the limiting complex of Np(IV). Unfortunately there are some experimental difficulties (see [95DEL] and the discussion on [79FED/PER] in the Appendix A), and the authors, that tried to use this methodology either did not succeed to measure the potential [84VAR/HOB], or only propose a very rough value [79FED/PER], or do not give enough information to check their interpretation [95DEL]. Our calculation (see the discussion on [79FED/PER] in the Appendix A) again is consistent with U-Np-Pu analogy. The redox potential of the equilibrium

$$NpO_2(CO_3)_3^{5-} + e^- + 2\ CO_2 <==> Np(CO_3)_5^{6-}$$

is then $E°(P_{CO_2} = 10^{-3.5}$ atm$) = 0.1 \pm 0.15$ V/SHE in 1 M Na_2CO_3 solution equilibrated with the air. $E°(P_{CO_2} = 1$ atm$) = 0.105$ V/SHE. From SIT regression [95DEL], $\varepsilon(Np(CO_3)_5^{6-}, Na^+) - \varepsilon(NpO_2(CO_3)_3^{5-}, Na^+) = -0.17 \pm$??? kg/mole. Using the $\varepsilon(NpO_2(CO_3)_3^{5-}, Na^+)$ selected in this review (-0.36 ± 0.08), $\varepsilon(Np(CO_3)_5^{6-}, Na^+) = -0.53 \pm$??? kg/mole. *THESE NUMBERS WILL BE (SLIGHTLY) CHANGED (SEE THE APPENDIX A) [95DEL], T INFLUENCE WAS ALSO MEASURED IN [95DEL]. NEW TABLE.*

The reduction of water seems to be a limitation to study the Np(IV)/Np(III) redox system.

5.3. Solubility measurements.

Rai and Ryan [85RAI/RYAN] have shown a good methodology to performed solubility measurement in neutral or low concentrated carbonate media. They conclude, that there is no evidence of any Np(IV) carbonate complex in these conditions. The present review completely agrees, that there is no evidence of any Np(IV) carbonate complex when the total carbonate concentration is less then 0.01 M at low ionic strength. Pratopo et col. published two papers [90PRA/MOR] [89MOR/PRA] where they tried to reproduce Rai and Ryan measurements; but they did not succeed, certainly because they did not use a proper methodology to handle Np(IV) in near neutral solutions. They end up with a set of solubility data, that is hardly correlated to any chemical parameters (see Appendix A), that are obtained in quite a narrow domain of chemical conditions. They even dare to propose some curve fitting results from these very scattered solubility data: this has no meaning at all. As already said at the beginning of this paragraph, this type of terrible results is now widely cited and used. To avoid this, the idea of Rai and Ryan [85RAI/RYAN] is very good: they calculated an "upper limit" of certain equilibrium constants corresponding to the formation of complexes, that probably do not exist. We use similar (appendix A) procedures. $Np(OH)_4^0$, $Np(CO_3)_4^{4-}$, $Np(CO_3)_5^{6-}$ and possibly soluble complexes of Np(V) seem to be enough to explain all the published data on "Np(IV)" hydroxide solubility in neutral and carbonate media: there is then no clear evidence of any other Np(IV) hydro carbonato complex.

The highly charged $Np(CO_3)_5^{6-}$ anion can be precipitated by many cations; but the work published on this subject cannot be used to determine the stoichiometry of the Np(IV) limiting complex (see the discussion on [71MOS5] and [77SAI/UEN] in the Appendix A).

Finally U-Np-Pu-(and probably Ce-Th Am) analogy seems to be enough to explain all published data. Hence $Np(CO_3)_5^{6-}$, $Np(CO_3)_4^{4-}$ and $Np(OH)_4^0$ complexes are probably formed in carbonate media. There is no evidence of other complexes, that does not mean that they do not exist. We have estimated formation constants of these Np complexes *EITHER THEY ARE consistent WITH U AND Pu ONES? OR THEY ARE A LITTLE TOO HIGH WICH INDICATES UNKNOWN COMPLEXES. I SUGGEST? IN BOTH CASES? TO RECOMMEND U AND Pu VALUES INSTEAD OF NO VALUE.*

Ce tableau est le projet de celui qui devrai apparaître dans le § VI.6.1.3 Np(IV) carbonate complexes du chapitre du livre discutant la sélection des données. Le tableau 5.3 sur les potentiels d'oxydo-réduction devra précéder le tableau "Table [79FED/PER]-2 [84VAR/HOB]-1", une fois que [95DEL] sera publié et éventuellement réinterprété. Les valeurs de potentiel d'oxydo réduction seront ensuite utilisées (comme dans ce "table") pour éventuellement proposer des valeurs de constantes de formation de complexes.

5.4. Possible complexes of Np(IV) in concentrated carbonate media

5.4.1. $M_{4+} + 4\ CO_3^{2-} \leftrightarrow M(CO_3)_4^{4-}$

M	Reference	lg K'	kg K°	method	conditions
U	[92GRE/FUG]		34.0±0.9	rev	I = 0
Np	[85RAI/RYAN]	< 38.5		sol	0.01 M ($HCO_3 + CO_3$), Na
Np	*[85RAI/RYAN]	< *38.4		*sol	0.01 M ($HCO_3 + CO_3$), Na
Np	[89MOR/PRA]	41.1±1.4	39.35	sol	NaHCO3 in contact with air
Pu	*[92CAP]		32.2[a]±1.0	*red, sp	I = 0

5.4.2. $M(CO_3)_4^{4-} + CO_3^{2-} \leftrightarrow M(CO_3)_5^{6-}$

M	Reference	lg K'	kg K°	Method	Conditions
Np	*[93LI/KAT]	<1.3±0.5	-1.45[b]	*sp	0.2 M Na_2CO_3, pH 10.8
Np	[95DEL]	1.5	-0.994[b]	sp	0.4 M Na^+, HCO_3^-, CO_3^{2-}
Np	[95DEL]	1.63	-1.002[b]	sp	0.6 M Na^+, HCO_3^-, CO_3^{2-}
Np	[95DEL]	1.80	-0.92[b]	sp	0.8 M Na^+, HCO_3^-, CO_3^{2-}
Np	[95DEL]	1.79	-1.018[b]	sp	1.0 M Na^+, HCO_3^-, CO_3^{2-}
Np	[95DEL]	2.2	-0.606[b]	sp	1.2 M Na^+, HCO_3^-, CO_3^{2-}

M	Reference	kg K°	Method	Conditions	Δε
U	[92GRE/FUG] (TDB review)	-1.12±0.3	SIT	I = 0	-0.13±0.11
Np	[95DEL]	-0.98[b]±0.20	SIT	I = 0	0.44±0.05
Np	[95CAP/VIT] from [95DEL] data	-1.35[b]±0.17	SIT	I = 0	-0.06±0.36
Pu	[92CAP]	-1.0[a]±0.2	SIT	I = 0	0.9±0.1
Pu	[95CAP/VIT] from [92CAP] data	-1.36[b]±0.2	SIT	I = 0	0.11±0.08

5.4.3. $M^{4+} + 5\ CO_3^{2-} \leftrightarrow M(CO_3)_5^{6-}$

M	Reference	lg K'	kg K°	Method	Conditions
Np	*[79FED/PER]	41.5±3.4	39.1±3.7	*red	1 M Na_2CO_3
Np	*[79FED/PER]	39.7±1.7	36.5±3.1	*red	1 M K_2CO_3
Np	*[84VAR/HOB]	39.4±1.7	36.1±3.1	*red	1 M K_2CO_3
Np	*[84VAR/HOB]	38.2±1.7	35.2±3.8	*red	2 M Na_2CO_3
Np	[85RAI/RYAN]	< 41.6		sol	0.01 M ($HCO_3 + CO_3$), Na
Np	*[85RAI/RYAN]	< 40.7		*sol	0.01 M ($HCO_3 + CO_3$), Na
Np	[95DEL]		38[c]±2	red	I = 0
U	[92GRE/FUG]		34±0.9		I = 0
Pu	*[92CAP]		32.2[a]±2	*red	I = 0

*Calculated or estimated in this review, [a]*THIS REVIEW ON Pu: NOT YET FINISHED,* [b]*REVIEWING OF THE SPECTROPHOTOMETRIC STUDY IN [95DEL] WILL PRODUCE NEW (BETTER) NUMBERS AND ALLOW FURTHER REINTERPRETATION OF OTHER PUBLISHED SPECTROPHOTOMETRIC STUDIES.* [c]*REVIEWING OF THE ELECTROCHEMICAL STUDY IN [95DEL] WILL PRODUCE NEW NUMBERS.*

5.5. No evidence of the following complexes

5.5.1. $Np^{4+} + 2\ OH^- + 2\ CO_3^{2-} \leftrightarrow Np(OH)_2(CO_3)_2^{2-}$

Reference	lg K'	Method	Conditions
*[85RAI/RYAN]	< 42	*sol	0.01 M (HCO3 + CO3), Na
[90PRA/MOR]	45.69±0.44	sol	0.01 M (HCO3 + CO3), Na

5.5.2. $Np^{4+} + 4\ OH^- + CO_3^{2-} \leftrightarrow Np(OH)_4CO_3^{2-}$

Reference	lg K'	Method	Conditions
*[85RAI/RYAN]	< 46	*sol	0.01 M (HCO3 + CO3), Na
[90PRA/MOR]	53.05±0.02	sol	0.1 to 2.2 M (NH4)2CO3

5.5.3. $Np^{4+} + 4\ OH^- + 2\ CO_3^{2-} \leftrightarrow Np(OH)_4(CO_3)_2^{4-}$

Reference	lg K'	Method	Conditions
*[85RAI/RYAN]	< 48	*sol	0.01 M (HCO3 + CO3), Na
[90PRA/MOR]	53.07±0.44	sol	0.01 M (HCO3 + CO3), Na

5.5.4. $Np^{4+} + 3\ CO_3^{2-} \leftrightarrow Np(CO_3)_3^{2-}$

Reference	lg K'	Method	Conditions
[85RAI/RYAN]	< 33,2	sol	0.01 M (HCO3 + CO3), Na
*[85RAI/RYAN]	< 36	*sol	0.01 M (HCO3 + CO3), Na
[89MOR/PRA]	37±1.2	sol	NaOH, lgpCO2 = -3,5

* calculated or estimated in this review

5.6. Redox potentials of Np in carbonate media

5.6.1. Np(V)/Np(IV)

Reference	E	ΔS	Method	Conditions
[79FED/PER]	0.1±*0.2		red	1 M Na2CO3
[95DEL]	0.51	-272±50	red	I = 0, 1 atm carbonic gas ?
[95DEL]	0.247		red	0.3 M Na2CO3, pH 10.22 ?
[95DEL]	0.234	-133	red	0.6 M Na2CO3, pH = 10.28 ?
[95DEL]	0.244	-169	red	1 M Na2CO3, pH = 10.10 ?
[95DEL]	0.228	-136	red	1.5 M Na2CO3, pH = 11.54 ?
*[95DEL]	*0.10±*0.06		red	I = 0, air conditions
*[95DEL]	*0.52±*0.06		red	I = 0, 1 atm carbonic gas

5.6.2. Np(IV)/Np(III)

Reference	E	ΔS	Method	Conditions
[79FED/PER]	-1.32±0.1		vlt	1 M K2CO3
[84VAR/HOB]	-1.3±0.1		vlt	1 M K2CO3
[84VAR/HOB]	-1.2±0.1		vlt	2 M Na2CO3

* calculated or estimated in this review

5.7. Np(IV) spectra in concentrated carbonate media.

The spectra are obtained from the publications written on the figures. The limiting complex is obtained in 0.6 M Na_2CO_3 solution, and at higher concentration [81WES/SUL] [84VAR/HOB] [93LI/KAT] [95DEL]. For $NaHCO_3$ see the discussion of [81WES/SUL] in the appendix A. It is clear that the limiting complex is dissociated in 0.2 M Na_2CO_3 solution [93LI/KAT] [95DEL]. Comparing the ratio of the two peaks around 700 nm, the dissociated complex might also be detected in $(NH_4)_2CO_3$ solutions [71MOS5] [77SAI/UEN].

Limiting and dissociated complex of Np(IV) from [95DEL]

Missing Figures are available on paper versions

click here

see also [96DEL/VIT]

where this figure is in the PDF file

Published spectra of Np(IV) in concentrated CO_3^{2-}/HCO_3^- solutions

Missing Figures are available on paper versions

click here

see also [96DEL/VIT]

where this figure is in the PDF file

6. Speciation.

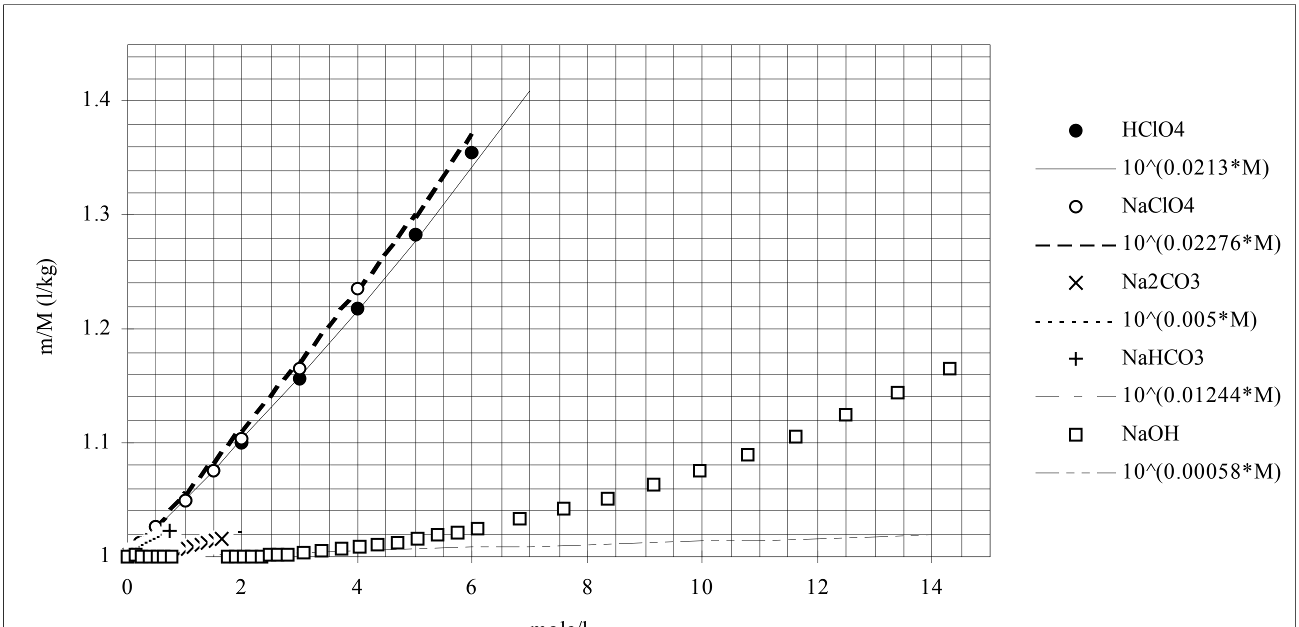
Nous recopions des extraits de calculs faits sous tableur Microsoft Excel. En tête sont indiquées les formules et constantes utilisées. Les calculs de speciation comportent diverses approximations sur les calculs d'activité et les conversions entre molalité molarité : elles sont explicitées. Quelques calculs de speciation en milieu Na_2CO_3 donnent les mêmes résultats que ceux faits par Hélène Capdevila (mêmes formules; mais logiciel différent). Il y a une erreur systématique (perceptible qu'en milieu très concentré), venant du fait qu'ici n'est pas pris en compte la variation de la masse totale de solvant (eau) due à la consommation d'eau lors de la réaction chimique de dissociation de CO_3^{2-}.

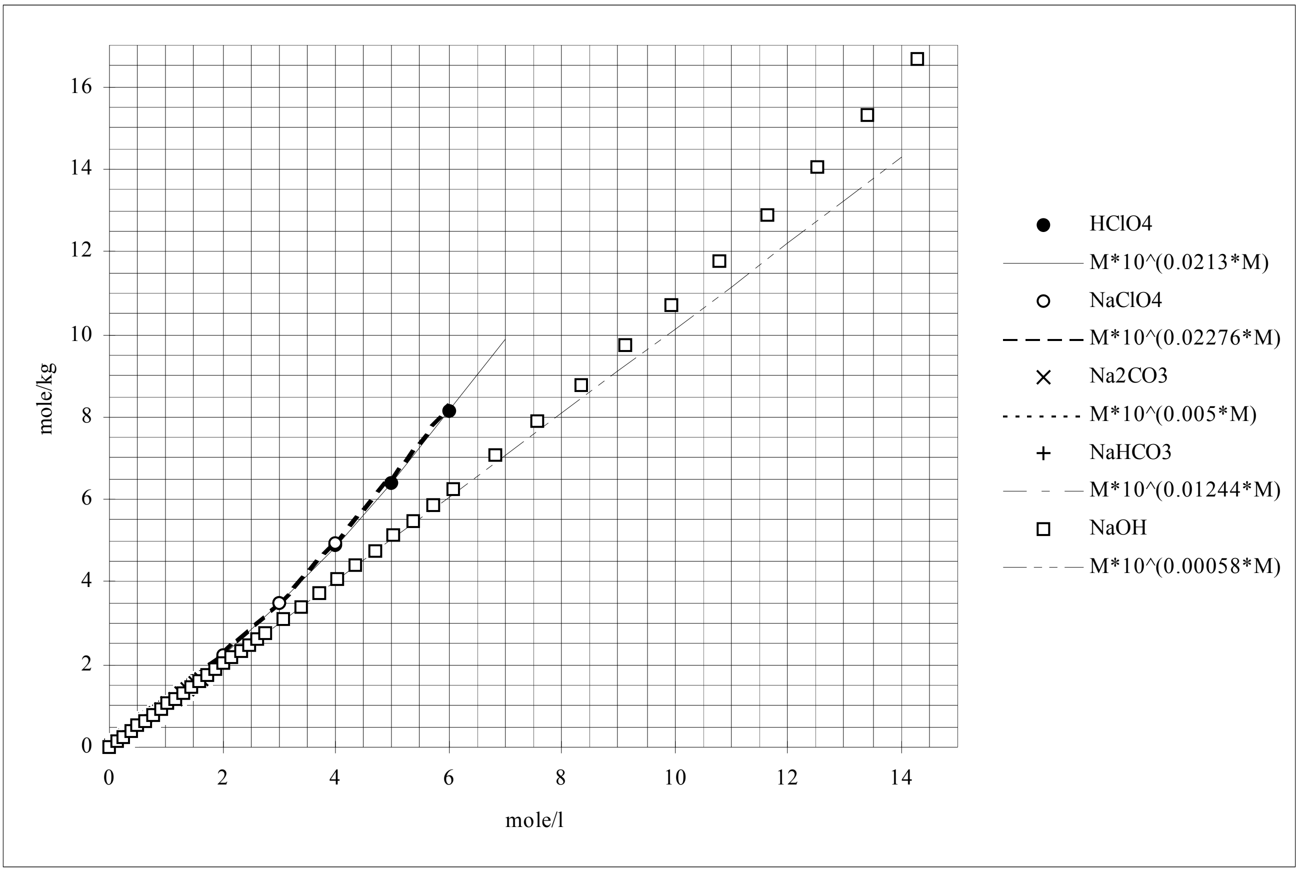
6.1. Conversion entre molalité et molarité.

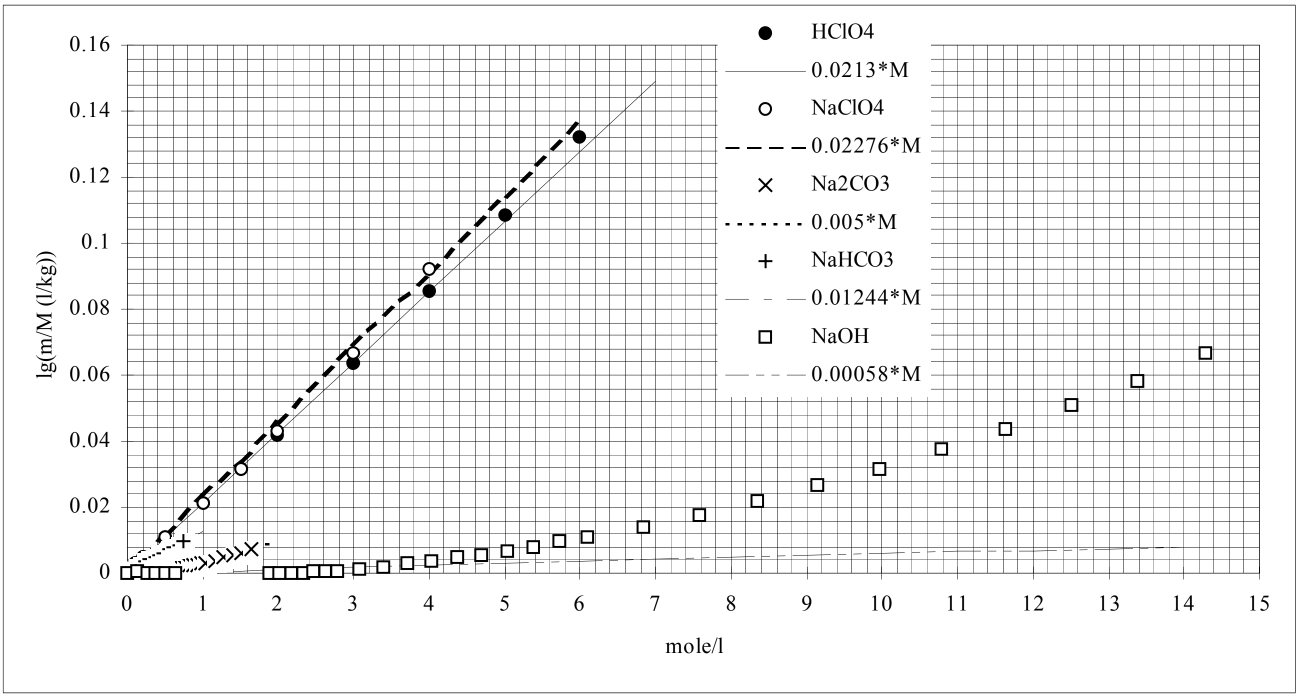
m = Molalité mole/kg M = Molarité mole/l
m = p M p = m/M l/kg
m #M 10^(r M) lg p # r M # q m

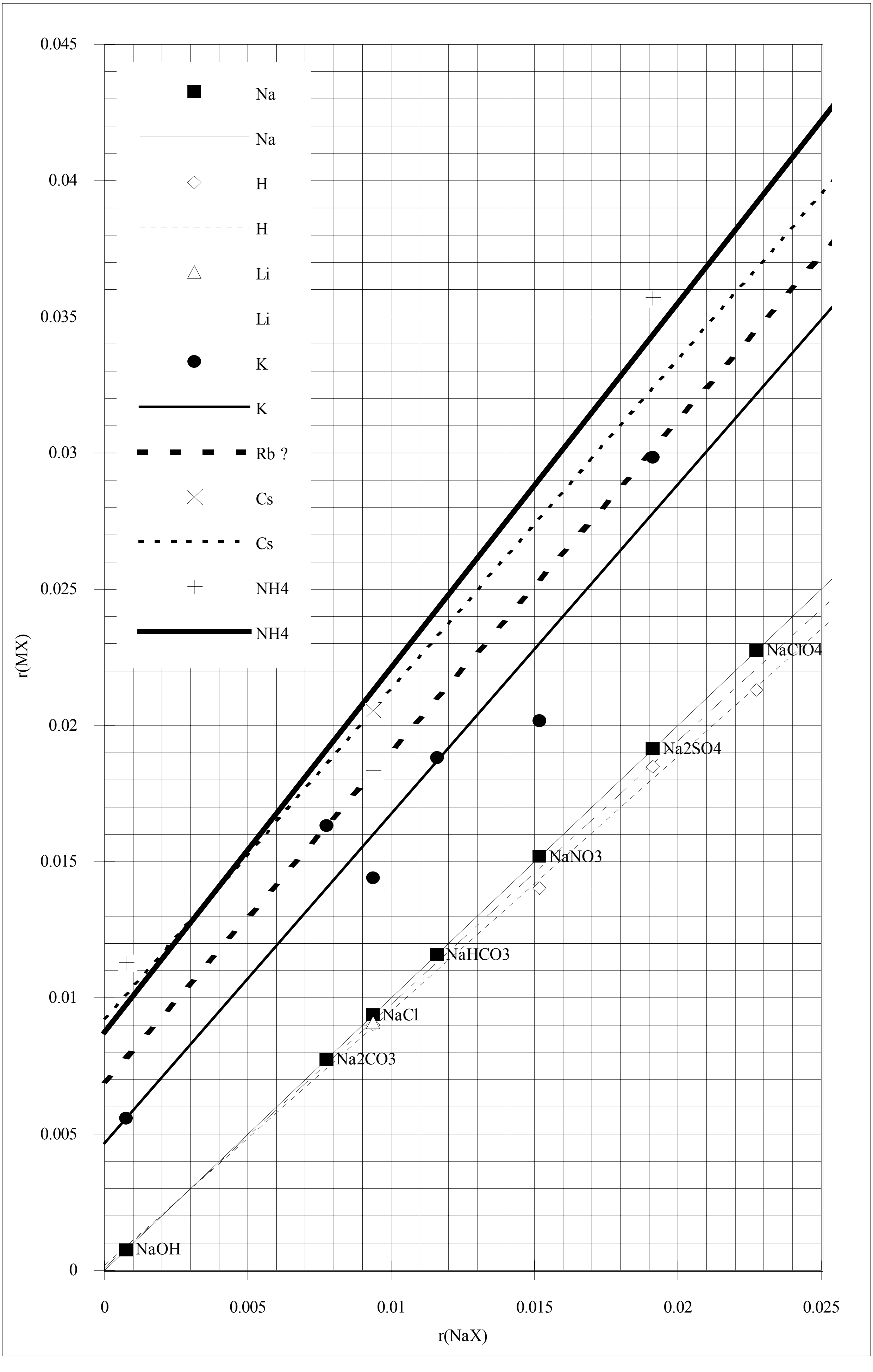
Valeurs de r et q à la molarité M_r.

		r	M_r	q			r	M_r	q
ClO_4	H	0.021	3.713	0.018	Cl	H	0.009	3.788	0.008
	Na	0.023	3.691	0.019		Li	0.009	3.563	0.008
CO_3	Na	0.008	3.5	0.007		Na	0.009	3.706	0.009
	K	0.016	3.56	0.014		K	0.014	3.742	0.013
HCO_3	Na	0.012	3.5	0.012		Cs	0.021	3.623	0.017
	K	0.019	3.5	0.016		NH_4	0.018	3.743	0.016
OH	Na	8E-04	3.71	8E-04	SO_4	H	0.018	3.729	0.016
	K	0.006	3.73	0.005		Na	0.019	3.5	0.016
	NH_4	0.011	3.706	0.01		K	0.03	3.5	0.023
						NH_4	0.036	3.716	0.026
					NO_3	H	0.014	3.538	0.013
						Na	0.015	3.981	0.013
						K	0.02	3.5	0.017



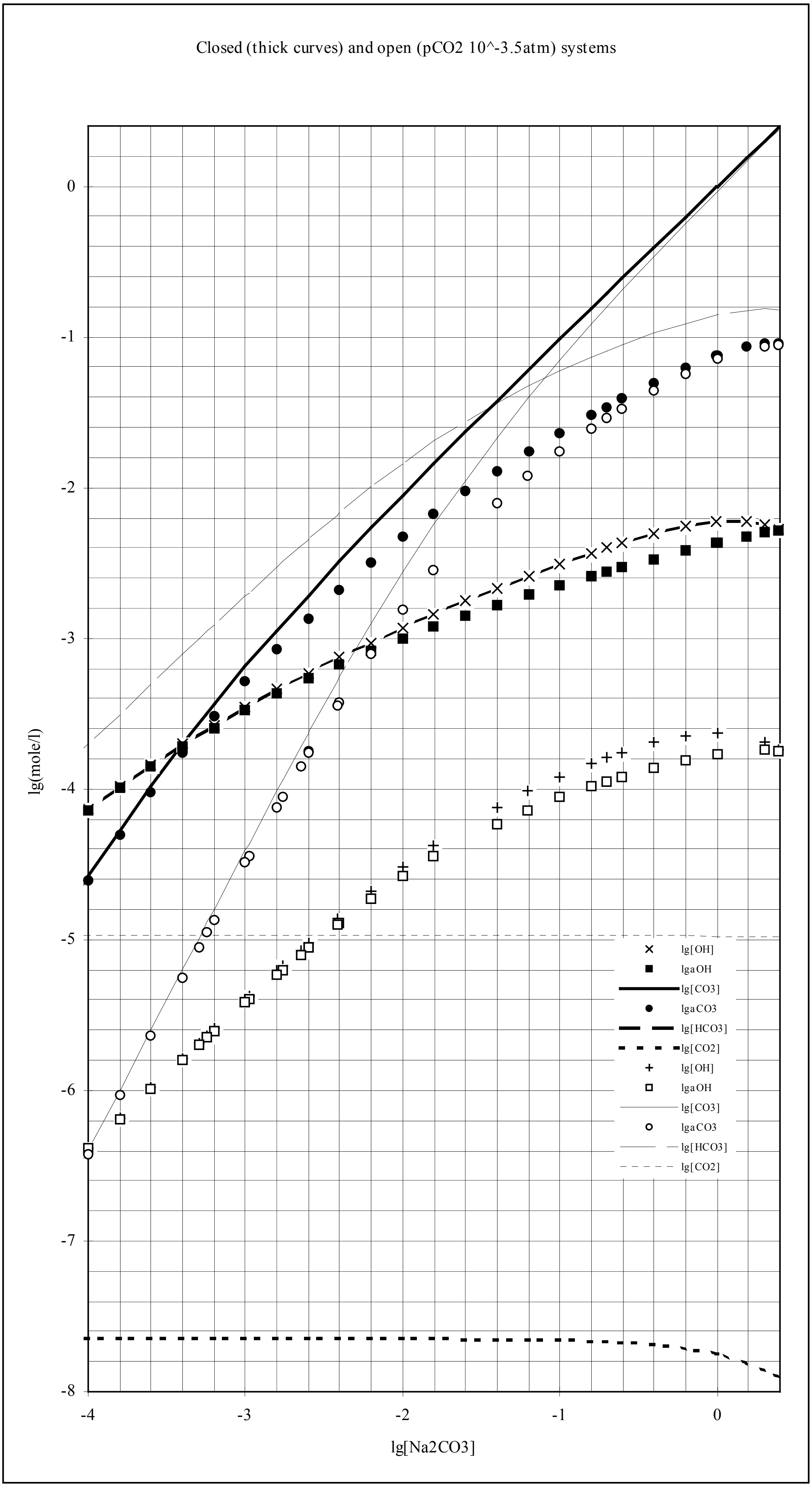

mole/kg
0
2
4
6
8
10
12
14
16
mole/l
0
2
4
6
8
10
12
14
HClO4
M*10^(0.0213*M)
NaClO4
M*10^(0.02276*M)
Na2CO3
M*10^(0.005*M)
NaHCO3
M*10^(0.01244*M)
NaOH
M*10^(0.00058*M)


lg(m/M (l/kg))
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
mole/l
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
HClO4
0.0213*M
NaClO4
0.02276*M
Na2CO3
0.005*M
NaHCO3
0.01244*M
NaOH
0.00058*M

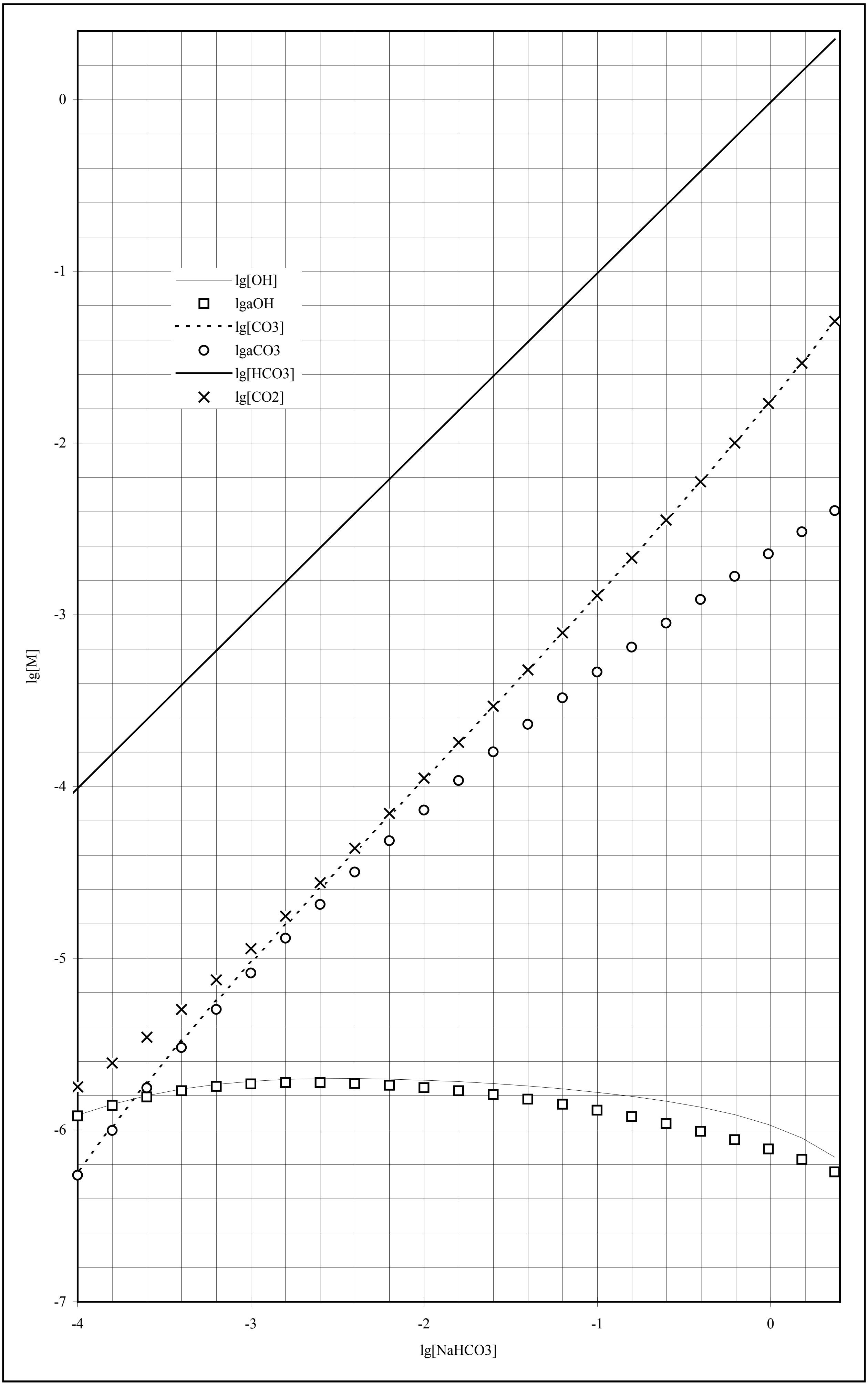

0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
r(MX)
0
0.005
0.01
0.015
0.02
0.025
r(NaX)
Na
Na
H
H
Li
Li
K
K
Rb ?
Cs
Cs
NH4
NH4
NaOH
Na2CO3
NaCl
NaHCO3
NaNO3
Na2SO4
NaClO4

6.2. Figures

6.2.1. Na_2CO_3

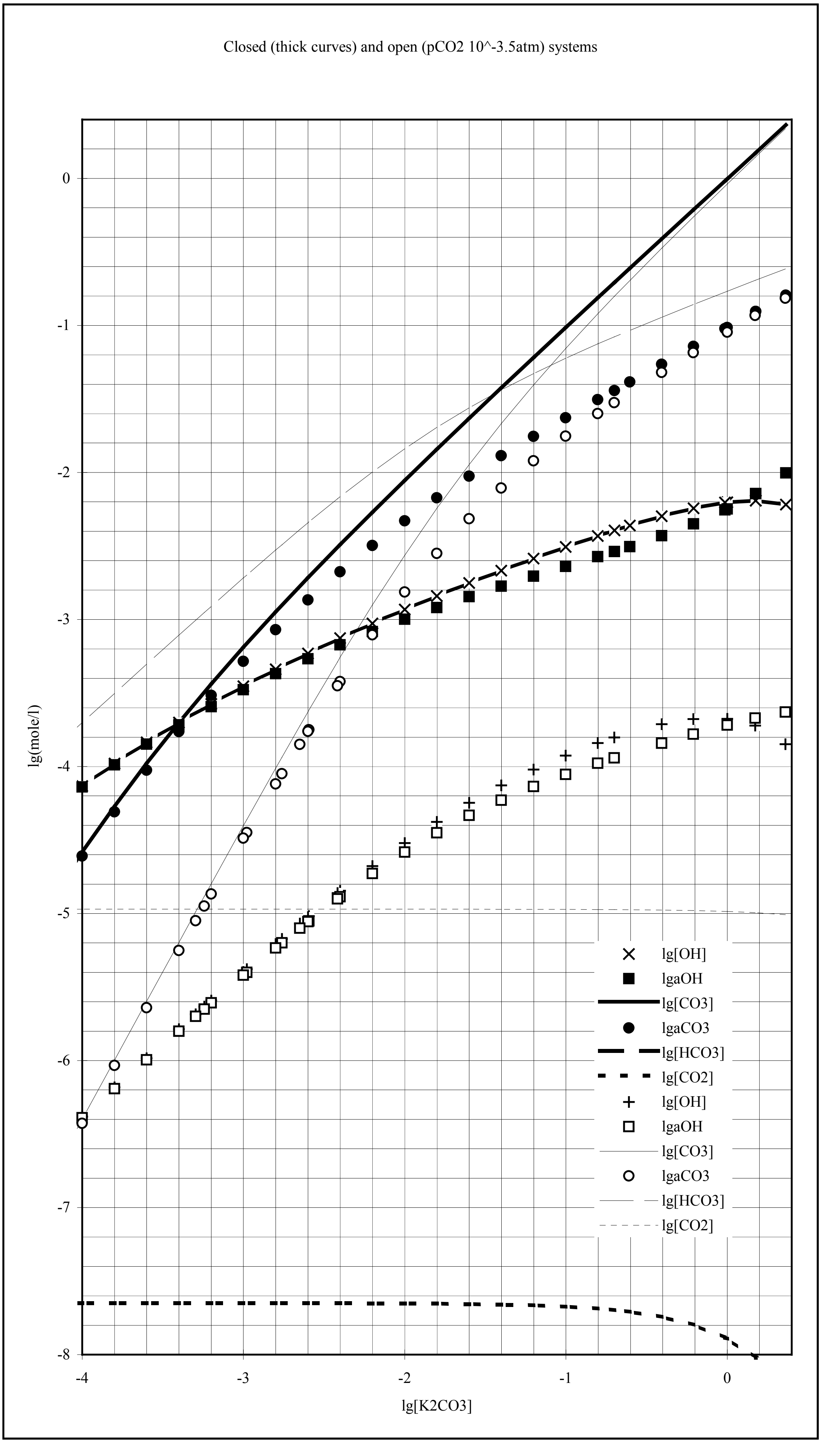


6.2.2. $NaHCO_3$

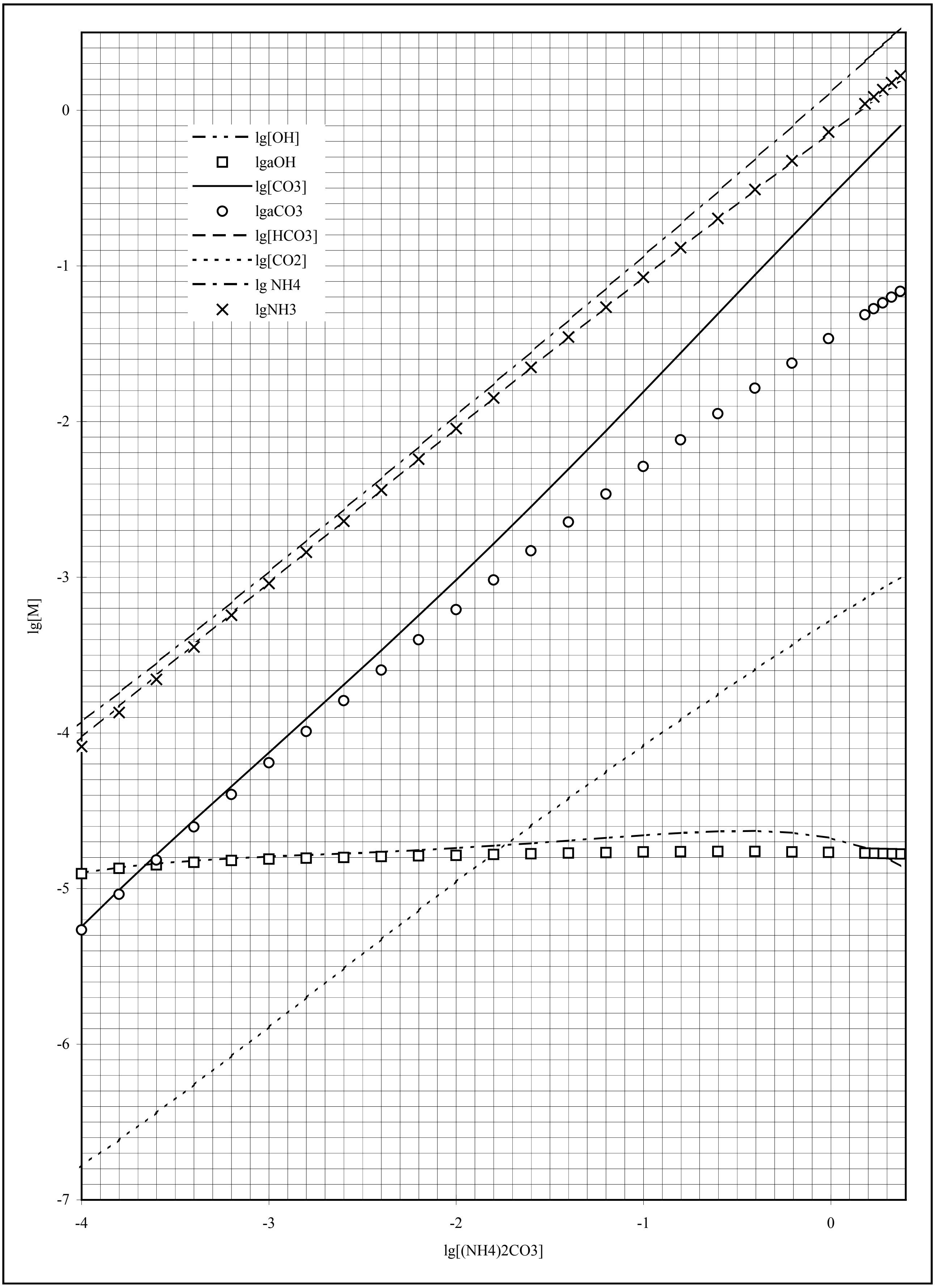


lg[OH]
lgaOH
lg[CO3]
lgaCO3
lg[HCO3]
lg[CO2]
lg[M]
lg[NaHCO3]
0
-1
-2
-3
-4
-5
-6
-7
-4
-3
-2
-1
0

6.2.3.K_2CO_3


Closed (thick curves) and open (pCO2 10^-3.5atm) systems
lg(mole/l)
0
-1
-2
-3
-4
-5
-6
-7
-8
-4
-3
-2
-1
0
lg[K2CO3]
× lg[OH]
■ lgaOH
lg[CO3]
● lgaCO3
lg[HCO3]
lg[CO2]
+ lg[OH]
□ lgaOH
lg[CO3]
○ lgaCO3
lg[HCO3]
lg[CO2]

6.2.4. $(NH_4)_2CO_3$


lg[OH]
lgaOH
lg[CO3]
lgaCO3
lg[HCO3]
lg[CO2]
lg NH4
lgNH3
lg[M]
0
-1
-2
-3
-4
-5
-6
-7
-4
-3
-2
-1
0
lg[(NH4)2CO3]

6.3 Calculs

6.3.1 Na_2CO_3

Missing pages (47-95/95) tabulate speciation details (including the paremeters to calculate them) in carbonate media.

They are available on paper version:

click here

6.3.2.$NaHCO_3$

6.3.3.K_2CO_3

6.3.4.$(NH_4)_2CO_3$

7. Réinterprétations