

XI Thorium Group 14 compounds and complexes

XI.1 Carbon compounds and complexes

XI.1.1 Solid thorium carbides

There have been two extensive reviews of the thermodynamics of the Th-C system by [1975RAN], [1984HOL/RAN], since which there has been little work on these compounds. Our treatment therefore lends fairly heavily on the latter review, with a few updates and corrections as appropriate.

There is a large corpus of data on the phase relationships and stability of the thorium carbides. Unfortunately, much of this information is conflicting, and it is still not possible to give many precise values for the thermodynamic properties of the carbides. These discrepancies may be due in part to the great difficulty encountered in preventing oxygen contamination of these materials.

XI.1.1.1 Phase diagram

There is little new information to add to the review of the somewhat conflicting information on the phase relationships given by [1984HOL/RAN], which gives the preferred phase diagram, the essential points of which are summarised below.

There are only two carbides stable at 1 bar pressure, the “monocarbide”, which has a wide range of homogeneity, even at low temperatures, and a “dicarbide” whose range of homogeneity is less certain. For neither carbide does the range of homogeneity include the stoichiometric ratio. A somewhat unusual feature of the system is that the miscibility gaps between the face-centred cubic of Th(cr) and “ThC”(cr) and between the “ThC(cr)” and “ThC₂(cr)” both close at high temperatures to form a single face-centred cubic phase, so that, by changing the temperature, it is possible to pass continuously from Th(cr, fcc) to ThC₂(cr, fcc).

In addition to these two carbides, Krupka [1970KRU] showed that the sesquicarbide is easily formed from a mixture of “ThC” and “ThC₂” heated to 1473 K at the relatively low pressure of 30 kbar. It has a body-centred cubic structure space group *I4/3d*, Pu₂C₃-type, isomorphous with the sesquicarbides of uranium, neptunium and plutonium with $a = (8.556 \pm 0.005) \text{ \AA}$. The relative ease of formation of this phase suggests that the Gibbs energy of the decomposition reaction $\text{Th}_2\text{C}_3(\text{cr}) \rightleftharpoons \text{ThC}(\text{cr}) + \text{ThC}_2(\text{cr})$ is only just positive at 1 bar pressure.

XI.1.1.2 Thorium monocarbide ThC_{1-x}(cr)

Thorium monocarbide has the NaCl face-centred cubic structure, space group $Fm\bar{3}m$, isomorphous with most of the actinide MX compounds. The limits of composition are still not well-defined, but up to *ca.* 1300 K probably extend from ThC_{0.67}(cr) to ThC_{0.97}(cr), the lattice parameter at room temperature varying from (5.303 ± 0.002) to $(5.346 \pm 0.002) \text{ \AA}$, see [1984HOL/RAN]. As noted earlier, at higher temperatures the

phase forms a continuous solid solution with both Th(cr) and “ThC₂”(cr). A more detailed literature account of the crystal structures of the thorium carbides is given by Kleykamp in his review of the general properties of thorium carbides for the Gmelin Handbook [1992KLE].

Low-temperature heat capacities have been measured by Harness *et al.* [1964HAR/MAT] from 1.8 to 4.2 K (uncharacterised sample), by Maurice *et al.* [1979MAU/BOU] from 2 to 15 K (ThC_{0.75}) and by Danan [1975DAN] from 2 to 300 K. The first two studies are mentioned for information only. Danan used two samples: one of overall composition ThC_{0.965}N_{0.015}O_{0.020}, which was used over the whole temperature range, and a second sample containing more oxygen (unspecified in [1975DAN], but *ca.* 2% ThO₂ according to [1984HOL/RAN]). The latter sample was certainly studied from 2 to 10 K, to confirm the low temperature data; it is not clear if any measurements at higher temperatures were made with this sample. Danan makes no mention of correction for the impurities in either sample, but merely attributes his given heat capacity and derived thermal functions to ThC(cr). For the moment we shall take these results to apply to the most carbon-rich composition of the monocarbide, giving ($S_m^\circ(\text{ThC}_{0.97}, \text{cr}, 298.15 \text{ K}) - S_m^\circ(\text{ThC}_{0.97}, \text{cr}, 0 \text{ K}) = (58.0 \pm 0.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).

A randomisation entropy corresponding to $-R(0.97 \ln 0.97 + 0.03 \ln 0.03)$ gives $S_m^\circ(\text{ThC}_{0.97}, \text{cr}, 0 \text{ K}) = (1.1 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and thus

$$S_m^\circ(\text{ThC}_{0.97}, \text{cr}, 298.15 \text{ K}) = (59.1 \pm 0.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

which with

$$C_{p,m}^\circ(\text{ThC}_{0.97}, \text{cr}, 298.15 \text{ K}) = (45.2 \pm 0.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

are the selected values. The uncertainty in the randomisation entropy takes account of the possibility that near the upper phase boundary, the ThC_{1-x} phase may contain some C₂ groups as well as carbon vacancies, and the uncertainty in the composition.

The high-temperature heat capacity of the monocarbide has not been measured, but following [1984HOL/RAN], has been estimated from that of UC and the low-temperature heat capacities:

$$[C_{p,m}^\circ]_{298.15\text{K}}^{2270\text{K}}(\text{ThC}_{0.97}, \text{cr}, T) = 46.02 + 25.52 \times 10^{-3} T - 18.83 \times 10^{-6} T^2 + 5.44 \times 10^{-9} T^3 - 6.28 \times 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

This has been refitted to three equations consistent with the NEA formalism, the lowest range of which is

$$[C_{p,m}^\circ]_{298.15\text{K}}^{1000\text{K}}(\text{ThC}_{0.97}, \text{cr}, T) = 50.067 + 1.27868 \times 10^{-2} T - 4.40301 \times 10^{-6} T^2 - 7.3671 \times 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

These data are mentioned for information only.

There have been two studies of the enthalpies of combustion of thorium monocarbides, by Huber *et al.* [1968HUB/HOL2] and Lorenzelli *et al.* [1971LOR/DIE], in both cases with a number of samples of different compositions. As it is apparent from

the discussion of the papers in Appendix A, there is excellent agreement on the enthalpy of formation near the ThC_{1.00} composition since [1968HUB/HOL2] give $\Delta_f H_m^\circ(\text{ThC}_{1.00}, \text{cr}, 298.15 \text{ K}) = -(123.8 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1}$ and [1971LOR/DIE] $\Delta_f H_m^\circ(\text{ThC}_{1.01}, \text{cr}, 298.15 \text{ K}) = -(126.4 \pm 10.5) \text{ kJ}\cdot\text{mol}^{-1}$. However, at other compositions the values of [1968HUB/HOL2] are consistently more negative than those of Lorenzelli *et al.*, even allowing for an uncertainty of 0.02 in the C/Th ratios.

Since the upper phase boundary of 'ThC' at 298.15 K is taken to be ThC_{0.97}, very small (for [1968HUB/HOL2], negligible) corrections have been made for the presence of the small amount of ThC_{1.94}(cr) presumably present in these samples, to give $\Delta_f H_m^\circ(\text{ThC}_{0.97}, \text{cr}, 298.15 \text{ K}) = -(123.8 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1}$ [1968HUB/HOL2] and $-(126.5 \pm 10.5) \text{ kJ}\cdot\text{mol}^{-1}$ [1971LOR/DIE]. The selected value is the weighted mean, with an increased uncertainty:

$$\Delta_f H_m^\circ(\text{ThC}_{0.97}, \text{cr}, 298.15 \text{ K}) = -(124.2 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

Both investigations show that the enthalpy of formation decreases very sharply in magnitude across the homogeneity range to *ca.* $-(40 \text{ to } 70) \text{ kJ}\cdot\text{mol}^{-1}$ at the thorium-rich phase boundary. For further details see the entries in Appendix A.

Holley *et al.* [1984HOL/RAN] give a detailed discussion of the two emf studies of the thorium potential in the single-phase ThC_{1-x}(cr), by Aronson and Sadofsky [1965ARO/SAD] (1073 to 1223 K) and by Satow [1967SAT2], (from 1000 to 1223 K), using the cell ThC_{1-x} + ThF₄|CaF₂ |ThF₄ + Th, which are outside the scope of the present review, as are the higher temperature measurements by [1989YAM/KOY] from 2060 to 2330 K, using mass-spectrometric Knudsen effusion.

Aronson and Sadofsky [1965ARO/SAD] and Satow [1967SAT2] also measured the thorium potentials on the ThC_{0.97}(cr)–ThC_{1.94}(cr) diphasic region, from the emf of the cell ThC_{0.97} + ThC_{1.94} + ThF₄|CaF₂ |ThF₄ + Th, but in view of the uncertainties in the thermal functions of ThC_{0.97}(cr), these data have not been used by this review.

The selected value for Gibbs energy of formation is:

$$\Delta_f G_m^\circ(\text{ThC}_{0.97}, \text{cr}, 298.15 \text{ K}) = -(124.5 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

XI.1.1.3 Thorium dicarbide

XI.1.1.3.1 Standard entropy, heat capacity and enthalpy of formation

Thorium dicarbide has three polymorphs. Because of their range of homogeneity, unique transformation temperatures cannot be given; those quoted below are for the phase in equilibrium with carbon. The low temperature form, stable below $(1690 \pm 40) \text{ K}$, is monoclinic, space group *C2/c* (CuO type) with $a = (6.692 \pm 0.003)$, $b = (4.223 \pm 0.003)$, $c = (6.744 \pm 0.003) \text{ \AA}$, $\beta = (103.12 \pm 0.11)^\circ$ [1968BOW/KRI] at room temperature, as determined by neutron diffraction. These results confirmed the lattice parameters and space group established earlier by Hunt and Rundle

[1951HUN/RUN] by X-ray and neutron diffraction. The second form, stable over the short temperature range from (1690 ± 40) to (1763 ± 45) K is tetragonal, space group $I4/mmm$ (CaC_2 type). The parameters (at 1723 K) vary from $a = (4.221 \pm 0.003)$, $c = (5.394 \pm 0.003)$ Å for the carbon-poor boundary to $a = (4.165 \pm 0.003)$, $c = (5.420 \pm 0.003)$ Å at the carbon-rich boundary [1976PIA/ZAU]. The form stable at higher temperatures has the cubic fluorite structure, space group $Fm\bar{3}m$, with the a parameter varying from (5.70 ± 0.01) to (5.806 ± 0.005) Å at 1823 K [1968BOW/KRI]. More detailed structural data on the three dicarbide polymorphs can be found in [1992KLE].

The limits of composition of these phases are still not well-defined; the significant variation in parameters observed by [1968BOW/KRI] and [1976PIA/ZAU] and others in the tetragonal β and cubic γ high temperature phases, suggests an appreciable range of composition in these polymorphs (as does the difference in the β - γ transition temperature for carbon-poor and carbon-rich samples). However there are a number of studies [1969SEA/KEG] [1971BEN/BAL] which suggest that the monoclinic α -phase has a negligible range of homogeneity below *ca.* 1573 K with the composition $\text{ThC}_{1.94}$ [1969BEN/STO].

Takahashi *et al.* [1965TAK/WES2] and Westrum *et al.* [1965WES/TAK2] have measured the low-temperature heat capacities of two samples of the dicarbide, with compositions of $\text{ThC}_{1.98}(\text{cr})$ and $\text{ThC}_{1.93}(\text{cr})$ respectively. The former sample probably contained some free carbon, but the consistent values of $(S_m^\circ(298.15 \text{ K}) - S_m^\circ(0 \text{ K}))$ of (68.6 ± 0.3) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from the two studies has been taken to refer to the $\text{ThC}_{1.94}(\text{cr})$ composition. The assumption that this phase contains randomly mixed C and C_2 groups then gives a randomisation entropy of $S_m^\circ(\text{ThC}_{1.94}, \text{cr}, 0 \text{ K}) = (1.9 \pm 0.3) \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, to give:

$$S_m^\circ(\text{ThC}_{1.94}, \text{cr}, 298.15 \text{ K}) = (70.5 \pm 0.4) \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

which with

$$C_{p,m}^\circ(\text{ThC}_{1.94}, \text{cr}, 298.15 \text{ K}) = (56.8 \pm 0.2) \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

are the selected values, where the uncertainties have been increased to allow for uncertainties in the compositions.

No high-temperature heat capacities have been measured, but Westrum *et al.* [1965WES/TAK2] estimated $C_{p,m}$ of the dicarbide by the procedure suggested by Krikorian [1962KRI] for estimating the heat capacity of carbides, to provide the following equation:

$$[C_{p,m}^\circ]_{298.15\text{K}}^{1700\text{K}}(\text{ThC}_{1.94}, \text{cr}, T) = 63.5 + 12.09 \times 10^{-3} T - 9.25 \times 10^5 T^{-2} \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Holley *et al.* [1984HOL/RAN] give another (five-parameter) estimate by comparison specifically with uranium dicarbide (which has a pronounced upward curvature in the heat capacity at high temperatures). For convenience, their equation has been re-fitted to two extended Kelley equations to conform to NEA usage

$$[C_{p,m}]_{298.15\text{K}}^{900\text{K}}(\text{ThC}_{1.94}, \text{cr}, T) = 61.00 + 2.62460 \times 10^{-2} T - 7.978 \times 10^{-6} T^2 - 1.0031 \times 10^6 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$[C_{p,m}]_{900\text{K}}^{1700\text{K}}(\text{ThC}_{1.94}, \text{cr}, T) = 194.418 - 1.5869 \times 10^{-1} T + 6.5061 \times 10^{-6} T^2 - 2.2169 \times 10^7 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

These equations have been used in the analysis of the Gibbs energy data, but are not selected.

Following [1984HOL/RAN], the enthalpies of the monoclinic to tetragonal and tetragonal to cubic transitions are estimated to be 2.1 and 10.4 kJ·mol⁻¹, at the respective temperatures of 1690 and 1763 K.

$$\Delta_{\text{trs}} H_{\text{m}}^{\circ}(\text{ThC}_2, \text{cr}, 1690 \text{ K}) = (2.1 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{trs}} H_{\text{m}}^{\circ}(\text{ThC}_2, \text{cr}, 1763 \text{ K}) = (10.4 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

The α - β transition involves only small crystallographic movements and is thus likely to be associated with only a small enthalpy change; the value for the β - γ transition is estimated from that for the similar transition in UC₂(cr). The heat capacities of the high temperature phases are estimated to have the same constant value:

$$[C_{p,m}]_{1690\text{K}}^{1763\text{K}}(\text{ThC}_2, \beta) = (83.7 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$[C_{p,m}]_{1763\text{K}}^{2500\text{K}}(\text{ThC}_2, \gamma) = (83.7 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

There have been two studies of the enthalpies of combustion of thorium dicarbides, by Huber *et al.* [1968HUB/HOL2] and Lorenzelli *et al.* [1971LOR/DIE]. [1968HUB/HOL2] studied two separate samples of ThC_{1.91}(cr), containing 0.07 and 0.02 wt% oxygen, which was assumed to be present as ThO₂(cr) or SiO₂(cr). This introduces an additional uncertainty into the results, since some of the oxygen, at least, was probably dissolved in the dicarbide phase, especially in the first sample – see Appendix A. The values obtained were $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{ThC}_{1.91}, \text{cr}, 298.15 \text{ K}) = -(124.3 \pm 7.5)$ and $-(125.1 \pm 5.4) \text{ kJ}\cdot\text{mol}^{-1}$.

These values are much less negative than those obtained by [1971LOR/DIE], given as $-(159.0 \pm 16.7) \text{ kJ}\cdot\text{mol}^{-1}$. Their sample was said to contain traces of monocarbide, but no other details are given of the oxygen content, or any corrections applied to the measured value – see Appendix A. The data from Huber *et al.* [1968HUB/HOL2] have been preferred, and their mean value is the selected enthalpy of formation. This is also taken to refer to the ThC_{1.94}(cr) composition, with an increased uncertainty:

$$\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{ThC}_{1.94}, \text{cr}, 298.15 \text{ K}) = -(124.7 \pm 7.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

These selected data give $\Delta_{\text{f}} G_{\text{m}}^{\circ}(\text{ThC}_{1.94}, \text{cr}, 298.15 \text{ K}) = -(126.7 \pm 7.5) \text{ kJ}\cdot\text{mol}^{-1}$.

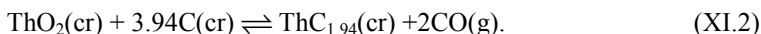
XI.1.1.3.2 Gibbs energy

There are a considerable number of studies to measure the Gibbs energy of the dicarbide. Three methods have been employed:

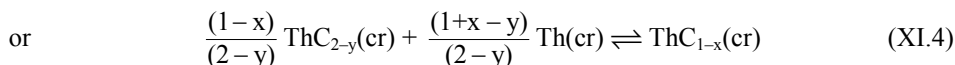
- the decomposition pressures from the vaporisation reaction, taken to be



- measurement of the CO(g) pressures in the reaction of thoria and graphite:



- emf studies using a CaF₂ solid electrolyte, which give Gibbs energies of the reactions:



However, the interpretation of most of these measurements is fraught with uncertainties, not only because the uncertainties in the phase boundaries of all the solid phases involved. The vapour over the dicarbide contains appreciable amounts of ThC₂(g) and ThC₄(g) as well as minor amounts of other gaseous carbides (see Section XI.1.2) while there is almost certainly some dissolution of oxygen into the dicarbide in Reaction (XI.2).

The experimental studies are summarised in Table XI-1. Since the thermal functions of the dicarbide are estimated we have, at this stage, just converted the relevant Gibbs energy measurements to derive the Gibbs energy of formation as a function of *T*, given in Table XI-1 in order to establish the consistency of the data. The results are shown in Figure XI-1. The data of [1981BES/LIN] have not been processed, since there seem to be differences, sometimes of a factor of *ca.* 100, between their tabulated and plotted pressures of CO(g) in Reaction (XI.3).

Aronson and Sadofsky [1965ARO/SAD] and Satow [1967SAT2] also measured the thorium potentials in the ThC_{0.97}(cr)-ThC_{1.94}(cr) diphasic region, from the emf of the cell ThC_{1-x} + ThC_{2-y} + ThF₄|CaF₂|ThF₄+Th, but in view of the uncertainties in the thermal functions of ThC_{0.97}(cr), these data have not been utilised by this review. The two studies [1964LOF/KRI], [1967WEE/MOR], which attempted to use absorption spectroscopy to determine the pressure of Th(g) in the carbon-saturated dicarbide system are subject to considerable uncertainty; the pressures of Th(g) over Th(l), which were used to calibrate the pressures, gave results for which the enthalpy of vaporisation was widely different from the accepted values. No individual pressures are given, so their results cannot be plotted in the figure. Short summaries of each paper are given in Appendix A.

Table XI-1: Gibbs energy studies to measure $\Delta_f G_m^\circ(\text{ThC}_{2-x})$.

Reference	Method	Reaction	Temperature range (K)	Derived $\Delta_f G_m^\circ((\text{XI.3}), T)$ ($\text{J}\cdot\text{mol}^{-1}$)
[1963LON/GRA]	Target effusion	(XI.1)	2278 – 2897	$-96452 - 1.74 T$
[1964ARO]	emf	(XI.3)	1073 – 1223	$-151613 + 30.88 T$
[1964EGA]	emf	(XI.3)	973 – 1243	$-156244 + 30.88 T$
[1964JAC/BAR]	Mass– spectrometric effusion	(XI.1)	2371 – 2642	$-160101 + 11.44 T$
[1964LOF/KRI]	Absorption spectroscopy	(XI.1)	2440 – 2772	see text
[1965ARO/SAD]	Emf	(XI.4)	1073 – 1223	see text
[1967SAT2]	Emf	(XI.3)	993 – 1223	$-146858 + 24.06 T$
[1967SAT2]	Emf	(XI.4)	993 – 1223	see text
[1967WEE/MOR]	Absorption spectroscopy	(XI.1)	2585 – 2689	
From $\text{ThO}_2(\text{cr}) + \text{C}(\text{cr})$ reaction				
[1927PRE/HIN]	Manometric	(XI.2)	2057 – 2494	$-242657 + 36.71 T$
[1964HOL/GRE]	Torsion effusion	(XI.2)	ca. 1560 – 1680	$-146130 + 22.52 T$
[1971HEI/DJE]	Manometric	(XI.2)	2156 – 2410	$-87826 - 20.21 T$
[1974DJE/DOD]	Thermogravimetry		2219 – 2319	$-94267 - 17.99 T$
[1976PIA/ZAU]	Manometric	(XI.2)	1738 – 2283	$-71026 + 35.65 T$
[1981BES/LIN]	Manometric (diaphragm deflection)	(XI.2)	1328 – 1976	Inconsistencies in paper – see text

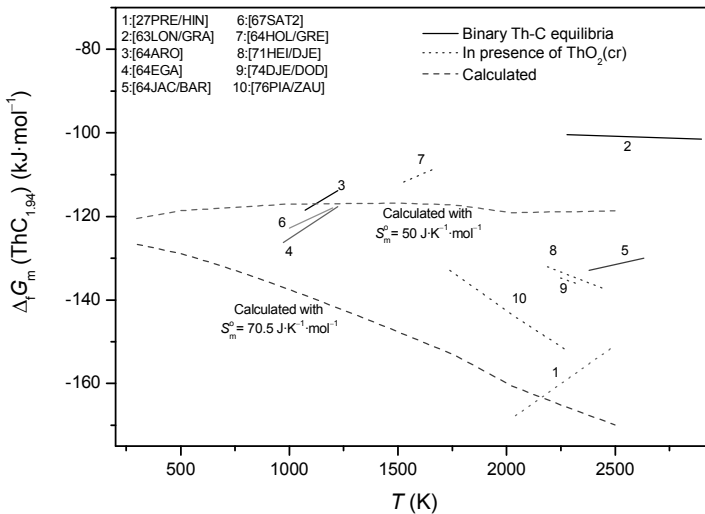
 Figure XI-1: Gibbs energy of formation of $\text{ThC}_{1.94}(\text{cr})$.


Figure XI-1 illustrates that $\Delta_f G_m^\circ(\text{ThC}_{2-x})$ calculated from various experimental studies are extremely scattered and that the Gibbs energy of formation calculated from the enthalpy of formation and entropy at 298.15 K and the estimated thermal functions, shows a marked discrepancy between the calorimetric values and most of the high temperature Gibbs energy measurements. Any plausible differences in the thermal functions would not resolve this discrepancy. As noted by [1984HOL/RAN], the main cause of this difference is the positive entropy of formation of $\text{ThC}_{1.94}(\text{cr})$. However, the measured entropies of $\text{ThC}_{0.91}(\text{cr})$ and $\text{ThC}_{1.94}(\text{cr})$ are very similar to those for $\text{UC}(\text{cr})$ and ‘ $\text{UC}_2(\text{cr})$ ’ [2003GUI/FAN], as would be expected, and it is very unlikely that $S_m^\circ(\text{ThC}_{1.94}, \text{cr}, 298.15 \text{ K})$ is as small as the value (*ca.* $50 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) required to give even approximate agreement with some of the Gibbs energy data. The causes of these large discrepancies in the data for the thorium carbides are far from clear. This review therefore selects only the data at 298.15 K, which are relatively consistent, and much less exposed to the problems of uncertain phase boundary composition and oxygen contamination that plague the high temperature measurements. Even so, any data for the carbides must clearly be used with due discretion.

XI.1.2 Gaseous thorium carbides

All the gaseous carbide species $\text{ThC}_n(\text{g})$ with $n=1$ to 6 have been identified mass-spectrometrically by Gupta and Gingerich [1980GUP/GIN], but all except $\text{ThC}_2(\text{g})$ and $\text{ThC}_4(\text{g})$ are very minor species, and only these latter will be considered in this review.

XI.1.2.1 Thorium dicarbide gas $\text{ThC}_2(\text{g})$

The vapour species in the ‘ $\text{ThC}_2(\text{cr})$ ’ + $\text{C}(\text{cr})$ region have been investigated mass-spectrometrically by Jackson *et al.* [1964JAC/BAR] (2371–2642 K), Kohl and Stearns [1974KOH/STE] (2686–2906 K), Gingerich [1978GIN] (2542–2710 K) and Gupta and Gingerich [1980GUP/GIN] (2417–2693 K), all using Knudsen effusion, and by Sasaki *et al.* [1971SAS/KUB] (2545–2780 K) using the Langmuir method.

The mass-spectrometric measurements show similar amounts of $\text{Th}(\text{g})$ and $\text{ThC}_2(\text{g})$ in the vapour around 2500 K, with $\text{ThC}_4(\text{g})$ also being present in smaller, but still appreciable amounts at the higher temperatures.

The agreement between all these investigations is quite good, in contrast to many other measurements on the condensed phases in the Th-C system. From the data of Jackson *et al.* [1964JAC/BAR], we obtain the following equation:



$$[\Delta_f G_m]_{2350\text{K}}^{2650\text{K}}((\text{XI.5}), T) = (67632 - 29.325 T)$$

while the study of Kohl and Stearns [1974KOH/STE] gives for the Gibbs energy of reaction:

$$[\Delta_f G_m]_{2628\text{K}}^{2906\text{K}}((\text{XI.5}), T) = (81046 - 31.430 \times T).$$

These data are appreciably more scattered than those of [1964JAC/BAR].

At 2640 K, where they overlap, these values differ by *ca.* 8.5 kJ·mol⁻¹, well within the uncertainty of the measurements. The paper by [1978GIN] deals mainly with the pressures of ThC₃(g); although data for Reaction (XI.5) were also obtained, there is insufficient detail in the paper for them to be included in the current analysis.

Gupta and Gingerich [1980GUP/GIN] also studied the gaseous thorium carbides mass-spectrometrically, using a mixture of ThC₂, UC₂, Rh and excess graphite heated to 2300–2700 K in a graphite-lined Ta effusion cell. They identified all the gaseous carbide species ThC_{*n*}(g) with *n* = 1 to 6. As noted in Appendix A, they do not report their results in sufficient detail for them to be analysed, but they do imply that their results for Reaction (XI.5) are close to those of Kohl and Stearns [1974KOH/STE].

It is difficult to derive any reliable thermodynamic data from the Langmuir measurements by Sasaki *et al.* [1971SAS/KUB] from 2545 to 2780 K. The authors derive the enthalpy of Reaction (XI.5) to be $\Delta_r H_m((\text{XI.5}), 2662 \text{ K}) = (108.0 \pm 19.7)$ kJ·mol⁻¹ from the variation of the ratio of the fluxes of ThC₂(g) to Th(g), the uncertainty not including those relating to the detector efficiency and ionisation cross-sections of Th(g) and ThC₂(g). This is noticeably larger than the corresponding values from the reasonably consistent effusion measurements of [1964JAC/BAR] and [1974KOH/STE] and is not considered further.

Molecular parameters for ThC₂(g) have been estimated by [1964JAC/BAR], [1974KOH/STE] and [1980GUP/GIN] who regarded Th–C₂ as being similar to Th–O, with a linear Th–C=C structure. However, there is now considerable evidence from *ab initio* calculations [1995ROS/BAL], [1996ROS/BAL] that the corresponding lanthanide dicarbides have a symmetrical fan-shaped C_{2v} structure. Very recently, Kovács and Konings [2008KOV/KON] have made similar calculations for ThC₂(g) and ThC₄(g). For ThC₂, they find that the most stable structure is a less symmetrical essentially L-shaped molecule (C_s symmetry), with Th–C bond lengths of 2.155 and 2.473 Å, and a C–C bond length of 1.287 Å. The corresponding Th–C–C angles are 88.1° and 60.6° (see Appendix A). As noted there, the effective charge on the Th atom is calculated to be 1.60, so the electronic contributions to the partition function for ThC₂(g) are assumed to be the same as those for ThO(g) (see Section VII.1.2 and Table E-1). [2008KOV/KON] also give the three calculated harmonic vibration frequencies (see Table E-1). The molecular parameters for ThC₂(g) lead to the calculated values $C_{p,m}^\circ(\text{ThC}_2, \text{g}, 298.15 \text{ K}) = (45.1 \pm 2.0)$ J·K⁻¹·mol⁻¹ and $S_m^\circ(\text{ThC}_2, \text{g}, 298.15 \text{ K}) = (285.3 \pm 4.0)$ J·K⁻¹·mol⁻¹

With these thermal functions, a third-law treatment of the data from [1964JAC/BAR] and [1974KOH/STE] gives $\Delta_f H_m(\text{ThC}_2, \text{g}, 298.15 \text{ K}) = (784.7 \pm 9.2)$ kJ·mol⁻¹ and (801.5 ± 8.1) kJ·mol⁻¹ respectively, where the uncertainties do not include those from the experimental difficulties (conversion from ion intensities to pressures, *etc.*) and those in the estimated electronic levels for ThC₂(g). However, the consistent

values of the entropy of the reaction $\text{Th}(\text{g}) + 2\text{C}(\text{cr}) \rightleftharpoons \text{ThC}_2(\text{g})$ derived from the vaporisation data are much smaller than those calculated from the thermal functions, (29.3 vs. 61.6 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 2500 K [1964JAC/BAR], 31.8 vs. 59.2 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 2796 K [1974KOH/STE]).

In view of this considerable discrepancy in the entropy values this review does not feel confident in selecting any thermodynamic data for $\text{ThC}_2(\text{g})$.

XI.1.2.2 Thorium tetracarbide gas $\text{ThC}_4(\text{g})$

Kohl and Stearns [1974KOH/STE] have also measured the pressures of $\text{ThC}_4(\text{g})$ in the vapour over $\text{ThC}_2(\text{cr}) + \text{C}(\text{cr})$. At 2700 K, the $\text{ThC}_4(\text{g})$ pressure is 15% of the thorium pressure, so this species cannot be neglected. Jackson *et al.* [1964JAC/BAR] do not report observing it in their measurements at lower temperatures and this is consistent with the data derived below.

From their recent *ab initio* calculations, Kovács and Konings [2008KOV/KON] found that $\text{ThC}_4(\text{g})$ has a symmetrical C_{2v} structure with two coplanar C–Th–C groups, one with Th–C = 2.365 Å, and a C–Th–C angle of 91.6°, and the second (inside the first) with Th–C = 2.532 Å, and a C–Th–C angle of 31.2° – see Appendix A for more details. Kovács and Konings [2008KOV/KON] also give the nine calculated harmonic vibration frequencies (see Table E-1). Since the effective charge on the Th atom in $\text{ThC}_4(\text{g})$ was calculated to be 1.66, the electronic contributions to the partition function for $\text{ThC}_4(\text{g})$ were assumed to be the same as those for $\text{ThO}(\text{g})$ (see Section VII.1.2 and Table E-1). This structure is, of course entirely different from the linear $\text{C}_2\text{–Th–C}_2$ assumed by Kohl and Stearns [1974KOH/STE], but is similar to that indicated for $\text{LaC}_4(\text{g})$ by [1997ROS/BAL]. The molecular parameters for fan-shaped $\text{ThC}_4(\text{g})$ molecule lead to the calculated values: $C_{p,m}^\circ(\text{ThC}_4, \text{g}, 298.15 \text{ K}) = (69.3 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $S_m^\circ(\text{ThC}_4, \text{g}, 298.15 \text{ K}) = (307.4 \pm 6.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

With these parameters, a third-law treatment of the data by [1974KOH/STE] gives $\Delta_f H_m^\circ(\text{ThC}_4, \text{g}, 298.15 \text{ K}) = (884.0 \pm 7.7) \text{ kJ}\cdot\text{mol}^{-1}$, where the uncertainty does not include those from the experimental difficulties (conversion from ion intensities to pressures, *etc.*) and those in the estimated electronic levels for $\text{ThC}_4(\text{g})$. The measurements of Gupta and Gingerich [1980GUP/GIN] suggest a somewhat lower proportion of $\text{ThC}_4(\text{g})$ in the gas phase, but agree with values calculated from the above enthalpy within the combined uncertainties. However, the entropy of the reaction $\text{Th}(\text{g}) + 4\text{C}(\text{cr}) \rightleftharpoons \text{ThC}_4(\text{g})$ at 2796 K derived from the vaporisation data of [1974KOH/STE], 89.9 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, is appreciably greater than that calculated from the thermal functions, 73.1 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

In view of this considerable discrepancy in the entropy values this review does not feel confident in selecting any values for $\text{ThC}_4(\text{g})$.

XI.1.3 Thorium carbonates

Experimental studies of thorium carbonates date back to the time of Berzelius [1829BER], who identified the formation of sparingly soluble basic thorium carbonates. Cleve [1874CLE] made an early identification of the compound $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}$, but formulated this as a double salt $\text{Th}(\text{CO}_3)_2 \cdot 3\text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. The strong complex formation between Th(IV) and the carbonate ion is apparent in the formation of a number of solid phases, some of which have been characterised by single-crystal X-ray diffraction [1975VOL/RIM2], [1975VOL/RIM3]. The formation of soluble carbonate complexes was indicated by the solubility of sparingly soluble thorium compounds such as monazite in carbonate media, a fact that was used in hydrometallurgical schemes for the recovery of thorium [2002ABD].

XI.1.3.1 Solid thorium carbonate compounds

In the earlier literature dealing with tetravalent actinides in carbonate solution, the formation of An(IV) carbonate solids like $\text{An}(\text{OH})_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ or $\text{AnOCO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ was postulated while solubility studies performed in the last decade have shown that the An(IV) hydrous oxides are the solubility limiting solid phases and do not transform into An(IV) carbonate or hydroxo-carbonate solids. An attempt of Ryabchikov *et al.* [1963RYA/VOL] to prepare the postulated solids $\text{Th}(\text{OH})_2\text{CO}_3 \cdot 6\text{H}_2\text{O}(\text{s})$ [1911CHA2] or $\text{ThOCO}_3 \cdot 8\text{H}_2\text{O}(\text{s})$ [1959RYA/GOL] in sodium and potassium carbonate solution led to the formation of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{cr})$ and $\text{K}_6[\text{Th}(\text{CO}_3)_5] \cdot 8\text{H}_2\text{O}(\text{cr})$, respectively. Dash *et al.* [2001DAS/KRI], [2002DAS/SIN] report the formation of $\text{ThOCO}_3(\text{s})$ and $\text{Th}(\text{CO}_3)_2(\text{s})$ by thermal decomposition of thorium oxalate hexahydrate, finally leading to $\text{ThO}_2(\text{cr})$. The authors report the characterisation by XRD, XPS, DTA/TGA and other methods. However, this review has doubts on the existence of these thorium compounds. The broad XRD bands ascribed to the intermediate $\text{ThOCO}_3(\text{s})$ and $\text{Th}(\text{CO}_3)_2(\text{s})$ compounds are at the same position as the peaks of the final product $\text{ThO}_2(\text{cr})$. The XRD patterns look very similar to those reported by [2000RAI/MOO] and [2003NEC/ALT] for microcrystalline $\text{ThO}_2(\text{s})$ with particle/crystallite sizes in the range 4–20 nm.

The following thorium carbonate solid phases have been synthesised in corresponding bicarbonate or carbonate solutions and characterised by chemical analysis, thermogravimetry and X-ray diffraction:

- $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{cr})$ [1963RYA/VOL], [1973DER/FAU], [1975VOL/RIM3],
- $\text{K}_6[\text{Th}(\text{CO}_3)_5] \cdot x\text{H}_2\text{O}(\text{cr})$, with $x = 8$ or 12 [1963RYA/VOL],
- $(\text{NH}_4)_6[\text{Th}(\text{CO}_3)_5] \cdot 3\text{H}_2\text{O}(\text{cr})$ [1961CHE/GOL],
- $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5] \cdot 4\text{H}_2\text{O}(\text{cr})$ [1973DER/FAU], [1975VOL/RIM2].

Thermodynamic data are not reported for these solids. However, the solubility data determined with $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ [1961LUZ/KOV2], [1973DER/FAU3]

allow the determination of the solubility constant at zero ionic strength (*cf.* Section XI.1.3.3) and the molar standard Gibbs energy of formation:

$$\Delta_f G_m^\circ (\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(8002.6 \pm 7.3) \text{ kJ} \cdot \text{mol}^{-1}.$$

XI.1.3.2 Aqueous thorium complexes with carbonate

Both qualitative and quantitative data are available. Only the quantitative data can be used to obtain thermodynamic parameters, but the qualitative information can in some cases be used to corroborate the quantitative conclusions, *e.g.* concerning the stoichiometry of complexes and the mode of coordination of the carbonate ligand. Quantitative determinations of the stoichiometry and equilibrium constants are described in the following section. These studies are complicated by the formation of sparingly soluble solid phases and the formation of ternary Th(IV)-hydroxide-carbonate species. This review will therefore begin with a short summary of the advantages and disadvantages of the various methods used to deduce the stoichiometry and equilibrium constants in the ternary Th(IV)-carbonate-water system.

The analysis of experimental data is facilitated if the ternary system is reduced to a "formal" three-component system by keeping the concentration of one component, A, constant and varying the other two, B and C. These data provide information on the stoichiometry of the complexes with respect to the two components that are varied and their conditional equilibrium constants. By repeating the investigation in new series of experiments where the concentration of A is still constant but with the values (A_1 , A_2 , A_3 *etc.*) in the different series, one can determine the stoichiometry with respect to A and the equilibrium constants for the ternary complexes. The choice of components in the thorium carbonate system depends on the pH region investigated; at low pH where the partial pressure of CO_2 can be measured it is practical to use $\text{CO}_2(\text{g})$ as one of the components, the other two being the concentrations of Th^{4+} and H^+ . The chemical equilibria are then formulated as:



The conditional equilibrium constants (for a given partial pressure p_{CO_2} of carbon dioxide) for these reactions are:

$${}^*K_{p,m,q} = \frac{\sum_n [\text{Th}_m(\text{OH})_q(\text{CO}_2)_n^{4m-q}][\text{H}^+]^q}{[\text{Th}^{4+}]^m} \quad (\text{XI.7})$$

where

$$\begin{aligned}
 {}^*K_{p,m,q} &= \frac{[\text{Th}_m(\text{OH})_q]^{4m-q} [\text{H}^+]^q}{[\text{Th}^{4+}]^m} + \frac{[\text{Th}_m(\text{OH})_q(\text{CO}_2)^{4m-q}] [\text{H}^+]^q}{[\text{Th}^{4+}]^m} \\
 &+ \frac{[\text{Th}_m(\text{OH})_q(\text{CO}_2)_2]^{4m-q} [\text{H}^+]^q}{[\text{Th}^{4+}]^m} + \dots \\
 {}^*K_{p,m,q} &= {}^*\beta_{m,q,0} + {}^*\beta_{m,q,1} p_{\text{CO}_2} + {}^*\beta_{m,q,2} p_{\text{CO}_2}^2 + \dots
 \end{aligned} \tag{XI.8}$$

The equilibrium constants ${}^*\beta_{m,q,n}$ for the species $\text{Th}_m(\text{OH})_q(\text{CO}_2)_n^{4m-q}$ refer to Reaction (XI.6). Details in the analysis of such data are given in [1961ROS/ROS]. The stoichiometry of the complexes in terms of the components is unique, but CO_2 is not bonded as such in the complexes but as HCO_3^- and/or CO_3^{2-} , for which $(\text{OH})(\text{CO}_2) \equiv \text{HCO}_3^-$ and $(\text{OH})_2(\text{CO}_2) \equiv \text{CO}_3^{2-}$. The so-called proton ambiguity makes it impossible to decide on the origin of the proton released in the complex formation reactions using potentiometric data. This means that one cannot distinguish *e.g.* between complexes such as $\text{Th}(\text{OH})(\text{HCO}_3)^{2+}$ and $\text{Th}(\text{CO}_3)^{2+}$. However, there are other experimental methods that allow such distinctions to be made, *e.g.* using the different vibration modes in HCO_3^- and CO_3^{2-} determined by Raman spectroscopy. Moreover, HCO_3^- is a very weak ligand compared to OH^- and CO_3^{2-} . For instance in the case of trivalent actinides and lanthanides, the formation constant of $\text{M}(\text{HCO}_3)^{2+}$ is 4–5 orders of magnitude lower than those of $\text{M}(\text{OH})^{2+}$ and $\text{M}(\text{CO}_3)^+$ [1981CIA/FER], [1985SPA], [2003GUI/FAN]. For tetravalent metal ions the difference is expected to be even larger, so the formation of Th(IV) bicarbonate complexes need not be taken into account.

Most investigations of carbonate complexation in the Th(IV) system have been made at such high pH that one cannot use measurements of the partial pressure of CO_2 . Many of these studies have been made using solubility measurements where the total concentration of Th(IV) is low. In order to facilitate the analysis of the experimental data it is practical to work with buffers of $\text{HCO}_3^-/\text{CO}_3^{2-}$ or $\text{CO}_3^{2-}/\text{OH}^-$ where the concentration of one of the buffer components is kept constant. However, this procedure has in general not been used, a fact that complicates the interpretation of the experimental data. A particular problem arises in the interpretation of solubility data. In these cases a unique chemical model cannot be obtained unless an assumption is made about the nuclearity of the complexes formed. Solubility data only give information on the charge of the species formed and there is no *a priori* reason to assume that there is only a single species with a particular charge; when interpreting the solubility data one in general assumes that only mononuclear species are formed, *cf.* Section VII.3.1.3. For bicarbonate and carbonate solutions and $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffers at C_{tot} above 0.1 M, where the solubility is rather high, this assumption is supported by EXAFS measurements [1997FEL/RAI], [2006ALT/NEC]. The EXAFS spectra of about 1 mM Th solutions do not provide any evidence for the formation of polynuclear thorium carbonate complexes under these conditions.

XI.1.3.2.1 Solubility of ThO₂(am, hyd) in carbonate solution and formation constants of ternary Th(IV)-hydroxide-carbonate complexes

Östhols *et al.* [1994OST/BRU], Rai *et al.* [1995RAI/FEL], Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI] and Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC], have performed solubility studies with hydrous thorium oxide as the solid phase, in order to determine the stoichiometry and equilibrium constants of the thorium complexes with carbonate. The possible variation of the solid phase, dried or aged ThO₂(am, hyd) or Th(OH)₄(am) precipitates, does not seem to have complicated the experiments as indicated by the good agreement between the solubility measured by different authors under comparable conditions, *cf.* the discussion in [2005ALT/NEC] Appendix A. The experimental solubility data in [1994OST/BRU] and [2005ALT/NEC] have been measured at constant ionic strength ($I = 0.5$ M), either in the presence of CO₂(g) at partial pressures of 0.1 and 1.0 bar, or in carbonate/bicarbonate buffer solutions, partly with additions of NaOH. In a very recent study Altmaier *et al.* [2006ALT/NEC] extended their measurements with carbonate/bicarbonate buffers to a wide range of ionic strength, $I = 0.1-4.0$ M (NaHCO₃-Na₂CO₃-NaCl). Rai *et al.* [1995RAI/FEL] measured the solubility of ThO₂(am, hyd) in NaHCO₃ and Na₂CO₃-NaOH solutions (up to high carbonate concentrations) of variable ionic strength. Based on this study, Felmy *et al.* [1997FEL/RAI] derived a model with Pitzer parameters for the complex Th(CO₃)₅⁶⁻ which was later extended to Na₂CO₃ solutions containing 0.1 M NaOH and 2.33 m or 4.67 m NaCl [1999FEL/RAI]. The experimental conditions of the solubility studies in [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], [2005ALT/NEC], [2006ALT/NEC], are summarised in Table XI-2. They cover widely varying conditions, a $-\log_{10}[\text{H}^+]$ range of 4–13, carbonate concentrations up to 2 M and ionic strength varying from $I = 0.1$ M to more than 6 M in Na₂CO₃ solutions and Na₂CO₃-NaCl mixtures.

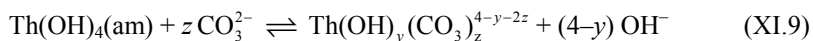
This review has made extensive use of the discussion in [2005ALT/NEC] that is the most comprehensive of the experimental studies so far; this paper also contains an analysis of some previous studies. The simultaneous evaluation of the different sets of experimental data at $I = 0.5$ M in [2005ALT/NEC] indicates that ThOH(CO₃)₄⁵⁻ and Th(OH)₂(CO₃)₂²⁻ are the most important ternary complexes while Th(OH)₂(CO₃)(aq), Th(OH)₃(CO₃)⁻ and Th(OH)₄(CO₃)₂²⁻ are of minor significance. According to the comprehensive test calculations in [2005ALT/NEC], binary carbonate complexes and other ternary complexes give no significant contributions to the solubility under the experimental conditions of [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI] and [2005ALT/NEC]; only upper limits could be derived for their formation constants. Altmaier *et al.* [2005ALT/NEC] demonstrated that the solubility data determined by different authors under different experimental conditions could be consistently described with a unique set of complexes and equilibrium constants. However this speciation model is not consistent with those of Östhols *et al.* [1994OST/BRU] and Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI] who proposed Th(CO₃)₅⁶⁻ as the dominant

complex at carbonate concentrations of 0.1–2.0 M and $\text{Th}(\text{OH})_3(\text{CO}_3)^-$ in near-neutral solutions of lower (bicarbonate) concentration.

Table XI-2: Experimental conditions of the available sets of solubility data with $\text{ThO}_2(\text{am, hyd})$ in carbonate solution (22–25°C).

Reference	Medium	I (mol·L ⁻¹)	Carbonate	pH range
[1994OST/BRU]	NaClO ₄ , CO ₂ (g)	0.5	$p_{\text{CO}_2} = 0.1$ bar	$-\log_{10}[\text{H}^+] = 4.6 - 7.4$
		0.5	$p_{\text{CO}_2} = 1.0$ bar	$-\log_{10}[\text{H}^+] = 4.1 - 6.3$
	Na(HCO ₃ -CO ₃ -ClO ₄)	0.5	$C_{\text{tot}} = 0.10$ M	$-\log_{10}[\text{H}^+] = 8.2 - 10.5$
[2005ALT/NEC]	NaCl, CO ₂ (g)	0.5	$p_{\text{CO}_2} = 0.1$ bar	$-\log_{10}[\text{H}^+] = 5.0 - 7.6$
		0.5	$p_{\text{CO}_2} = 1.0$ bar	$-\log_{10}[\text{H}^+] = 4.4 - 6.6$
	Na(HCO ₃ -CO ₃ -OH-Cl)	0.5	$C_{\text{tot}} = 0.10$ M	$-\log_{10}[\text{H}^+] = 8.7 - 13.0$
		0.5	$C_{\text{tot}} = 0.04$ M	$-\log_{10}[\text{H}^+] = 8.7 - 12.5$
		0.5	$C_{\text{tot}} = 0.015$ M	$-\log_{10}[\text{H}^+] = 8.7 - 13.0$
	[2006ALT/NEC]	Na ₂ CO ₃ -NaOH	var.	$C_{\text{tot}} = 0.25 - 2.0$ M
NaHCO ₃ -Na ₂ CO ₃		0.1–0.3	$C_{\text{tot}} = 0.1$ M	$-\log_{10}[\text{H}^+] = 8.7 - 10.8$
		0.1	$C_{\text{tot}} = 0.02$ M	$-\log_{10}[\text{H}^+] = 8.9 - 10.2$
		0.5	$C_{\text{tot}} = 0.02$ M	$-\log_{10}[\text{H}^+] = 8.7 - 10.6$
		2.0	$C_{\text{tot}} = 0.02$ M	$-\log_{10}[\text{H}^+] = 8.5 - 10.5$
4.0	$C_{\text{tot}} = 0.02$ M	$-\log_{10}[\text{H}^+] = 8.6 - 10.0$		
[1995RAI/FEL] and [1997FEL/RAI]	Na ₂ CO ₃ -NaOH	3.0–3.5	$C_{\text{tot}} = 1.0$ M	$[\text{OH}^-] = 0.01 - 0.5$ M
	Na ₂ CO ₃ -NaOH	var.	$C_{\text{tot}} = 0.001 - 2.0$ M	$[\text{OH}^-] = 0.1$ M
[1999FEL/RAI]	NaHCO ₃	var.	$C_{\text{tot}} = 0.01 - 0.25$ M	$-\log_{10}[\text{H}^+] = 8.6 - 9.5$
	Na ₂ CO ₃ + 2.3 m NaCl + 0.1 M NaOH	var.	$C_{\text{tot}} = 0.1 - 2.3$ M	$[\text{OH}^-] = 0.1$ M
		Na ₂ CO ₃ + 4.7 m NaCl + 0.1 M NaOH	var.	$C_{\text{tot}} = 0.1 - 2.3$ M

The equilibrium constants $\log_{10} K_{s,1yz}^{\circ} = (\log_{10} K_{s,0}^{\circ} + \log_{10} \beta_{1yz}^{\circ})$ derived by the different authors from their solubility studies with $\text{ThO}_2(\text{am, hyd})$ are given in Table XI-3¹. The notation 1yz refers to the stoichiometric coefficients in Eqs (XI.9) and (XI.10):



The solubility constants, $\log_{10} K_{s,0}^{\circ}$, selected in this review for dried or aged $\text{ThO}_2(\text{am, hyd})$ were combined with $\log_{10} K_{s,1yz}^{\circ}$ to calculate the formation constants of different species, $\log_{10} \beta_{1yz}^{\circ}$, according to the generalised reactions:

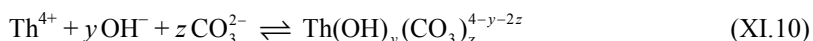


Table XI-3: Equilibrium constants for thorium complexes with carbonate relevant in solubility studies with dried or aged $\text{ThO}_2(\text{am, hyd})$ at 22–25°C. (Uncertainties are given as 2σ).

Complex (1yz)	$\log_{10} K_{s,1yz}$ ($I = 0.5 \text{ M}$)	$\log_{10} K_{s,1yz}^{\circ}$	$\log_{10} \beta_{1yz}^{\circ}$ ^a	Reference
(105) = $\text{Th}(\text{CO}_3)_5^{6-}$	< -13.2	< -16.6	< 31.0	[2005ALT/NEC]
	-12.9 ± 0.4	-16.4 ± 0.4	31.6 ± 0.6	[1994OST/BRU]
		-18.4	29.1 ± 0.9	[1997FEL/RAI]
			31.0 ± 0.7	This review ^b
(114) = $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$	-10.0 ± 0.1	-12.0 ± 0.2	35.6 ± 0.5	[2005ALT/NEC]
(121) = $\text{Th}(\text{OH})_2\text{CO}_3(\text{aq})$	-17.5 ± 0.2	-17.1 ± 0.3	30.5 ± 0.6	[2005ALT/NEC]
(122) = $\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$	-11.2 ± 0.1	-10.8 ± 0.2	36.8 ± 0.5	[2005ALT/NEC]
(131) = $\text{Th}(\text{OH})_3(\text{CO}_3)^-$	-9.7 ± 0.5	-9.3 ± 0.5	38.3 ± 0.7	[2005ALT/NEC]
	-7.6 ± 0.3 ^c	-7.2 ± 0.3 ^c	40.8 ± 0.6 ^c	[1994OST/BRU]
(141) = $\text{Th}(\text{OH})_4(\text{CO}_3)_2^{2-}$	-7.2 ± 0.3	-7.2 ± 0.3	40.4 ± 0.6	[2005ALT/NEC]

a: The formation constants $\log_{10} \beta_{1yz}^{\circ}$ for the reactions $\text{Th}^{4+} + y \text{OH}^- + z \text{CO}_3^{2-} \rightleftharpoons \text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z}$ are calculated according to: $\log_{10} \beta_{1yz}^{\circ} = \log_{10} K_{s,1yz}^{\circ} - \log_{10} K_{s,0}^{\circ}$ with the $\log_{10} K_{s,0}^{\circ}$ values calculated by this review: $\log_{10} K_{s,0}^{\circ} = -(47.6 \pm 0.5)$ [2005ALT/NEC], $-(48.0 \pm 0.5)$ [1994OST/BRU], or $-(47.5 \pm 0.9)$ selected by for aged $\text{ThO}_2(\text{am, hyd})$.

b: Evaluated in Section XI.1.3.2.2.

c: Based on high Th concentrations caused by colloidal / polymeric species (*cf.* discussion below and in Appendix A).

¹ As hydrous thorium oxide ($\text{ThO}_2(\text{am, hyd}) = \text{ThO}_2 \cdot x \text{H}_2\text{O}(\text{am})$ with $x = 2.4-2.5$ [1994OST/BRU], [2002NEC/MUL]) has a stoichiometry close to $\text{Th}(\text{OH})_4(\text{am})$, it is more convenient to write the reactions with $\text{Th}(\text{OH})_4(\text{am})$ as component rather than as: $\text{Th}(\text{OH})_4(\text{am, hyd}) + 2\text{H}_2\text{O}(\text{l}) + z \text{CO}_3^{2-} \rightleftharpoons \text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z} + (4-y)\text{OH}^-$, because particularly at high ionic strength, the term $2 \log_{10} a_w$ would have a significant effect on ionic strength corrections.

Östholms *et al.* [1994OST/BRU], and Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC] used the SIT approach for ionic strength corrections. The ion interaction coefficient for the complex $\text{Th}(\text{CO}_3)_5^{6-}$ is set equal to the known value of the analogous U(IV) complex, $\varepsilon(\text{Th}(\text{CO}_3)_5^{6-}, \text{Na}^+) = \varepsilon(\text{U}(\text{CO}_3)_5^{6-}, \text{Na}^+) = -(0.30 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ [2003GUI/FAN] and the value of $\varepsilon(\text{ThOH}(\text{CO}_3)_4^{5-}, \text{Na}^+) = -(0.22 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$ has been derived from $\log_{10} K_{s,114}$ values in 0.1–0.4 M NaCl ($\Delta\varepsilon = (0.22 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$) [2006ALT/NEC]. For the other complexes it is not possible to evaluate simultaneously the equilibrium constants and SIT coefficients from the available data. Therefore the unknown ion interaction coefficients $\varepsilon(\text{Na}^+, \text{Th}(\text{OH})_y(\text{CO}_3)_z^{4-y-2z})$ have been estimated from known values for actinide complexes of analogous charge and similar size [2005ALT/NEC] (Table XI-4). Because the uncertainties of estimated SIT coefficients should not exceed $\pm 0.2 \text{ kg}\cdot\text{mol}^{-1}$, the extrapolation of equilibrium constants at $I = 0.5 \text{ M}$ to zero ionic strength should have a relatively small error.

Table XI-4: SIT coefficients for Th(IV) carbonate and hydroxide-carbonate complexes estimated from charge type analogues [2005ALT/NEC] except otherwise stated.

<i>i</i>	<i>j</i>	$\varepsilon(i, j) \text{ (kg}\cdot\text{mol}^{-1}\text{)}$
$\text{Th}(\text{CO}_3)_5^{6-}$	Na^+	-0.30 ± 0.15^a
$\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$	Na^+	-0.25 ± 0.20 -0.22 ± 0.13^b
$\text{Th}(\text{OH})_2(\text{CO}_3)(\text{aq})$	$\text{Na}^+, \text{Cl}^-, \text{ClO}_4^-$	0
$\text{Th}(\text{OH})_2(\text{CO}_3)_2^{2-}$	Na^+	-0.1 ± 0.2
$\text{Th}(\text{OH})_3(\text{CO}_3)^-$	Na^+	-0.05 ± 0.20
$\text{Th}(\text{OH})_4(\text{CO}_3)^{2-}$	Na^+	-0.1 ± 0.2

a: $\varepsilon(\text{U}(\text{CO}_3)_5^{6-}, \text{Na}^+)$ from [2003GUI/FAN].

b: Experimental value from [2006ALT/NEC].

The thermodynamic model of Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI] is based on Pitzer's ion interaction approach including binary and ternary parameters for the complex $\text{Th}(\text{CO}_3)_5^{6-}$ (*cf.*, Appendix A review of [1997FEL/RAI]). Accordingly, the value of $\log_{10} K_{s,105}^\circ$ is not directly comparable to that of [1994OST/BRU].

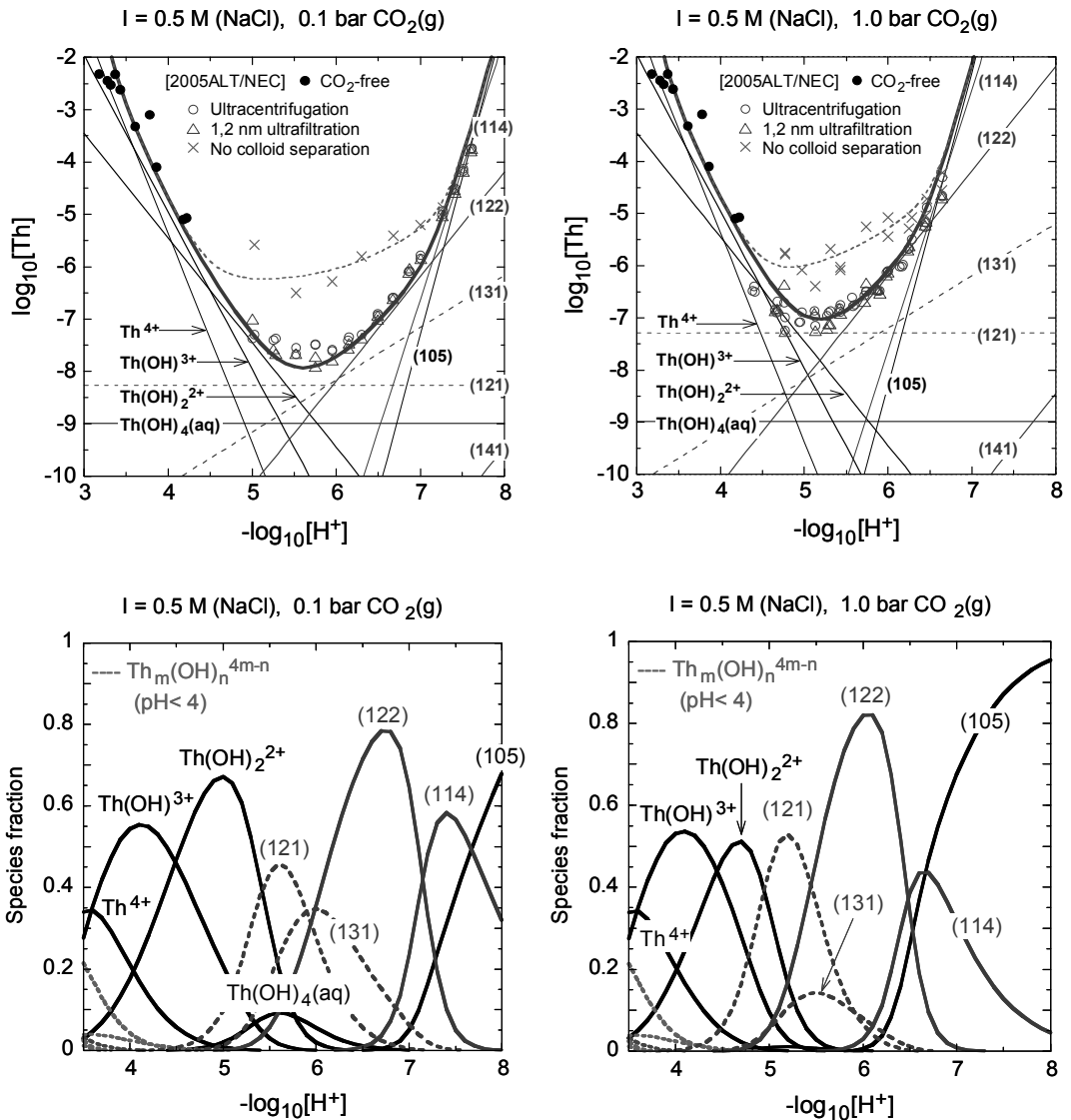
The binary and ternary complexes (Table XI-3) give reliable predictions of the solubility of $\text{ThO}_2(\text{am}, \text{hyd})$ in carbonate solutions as is demonstrated in the examples that follow. The equilibrium constant values for the ternary complexes in Table XI-3 are those proposed by [2005ALT/NEC] and the value for $\text{Th}(\text{CO}_3)_5^{6-}$ is that selected by this review. They are used together with the SIT coefficients in Table XI-4 to compare the calculated and experimental solubility data for all studies. For a better survey of the aqueous speciation, the corresponding speciation diagrams are also calculated, *cf.* Figure XI-2 and Figure XI-3.

The analysis of the experimental data in the thorium-carbonate system requires information on the equilibrium constants in the binary Th(IV)-hydroxide system. Therefore calculation of ThO₂(am, hyd) solubility in carbonate solution included hydrolysis constants selected in the present review and the solubility constants $\log_{10} K_{s,0}^{\circ}$ recalculated in the present review for dried or aged ThO₂(am, hyd) from the solubility data determined in the same study in carbonate-free solutions $\log_{10} K_{s,0}^{\circ} = -(47.6 \pm 0.5)$ [2005ALT/NEC] and $-(48.0 \pm 0.5)$ [1994OST/BRU]. For the evaluation of studies where only solubility data in carbonate solution are reported [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], [2006ALT/NEC] the value selected by this review for aged ThO₂(am, hyd), $\log_{10} K_{s,0}^{\circ} = -(47.5 \pm 0.9)$, is used.

XI.1.3.2.1.1 Solubility studies under CO₂(g)

The close agreement between the calculations based on the estimated SIT coefficients in Table XI-4 and data of [2005ALT/NEC] is not surprising since Altmaier *et al.* used these data in their evaluation. The solubility study of Östhols *et al.* [1994OST/BRU] under CO₂(g) partial pressures of 0.1 and 1.0 bar shows evidence for the formation of polynuclear ternary complexes or colloids. The thorium concentrations measured in the range pH = 4.6–6.5 after 220 nm filtration are comparable to those measured by Altmaier *et al.* [2005ALT/NEC] under the same conditions without removing colloidal or polynuclear species (crosses in Figure XI-2). However, considerably lower Th concentrations were obtained after 1.2 nm ultrafiltration and ultracentrifugation [2005ALT/NEC], indicating that the concentrations in [1994OST/BRU] for the pH region 4.6 to 6.5 do not refer to Th(OH)₄(aq) and Th(OH)₃(CO₃)⁻ but to large polymers or colloids (*cf.* discussion of [1994OST/BRU] in Appendix A).

Figure XI-2: Solubility of $\text{ThO}_2(\text{am, hyd})$ and speciation under 0.1 and 1.0 bar $\text{CO}_2(\text{g})$ in 0.5 M NaCl [2005ALT/NEC]. The calculations are based on the equilibrium constant and SIT coefficients selected in the present review and the solubility constants calculated from the data in carbonate-free solutions, $\log_{10} K_{s,0}^\circ = -(47.6 \pm 0.5)$. The dotted curves are calculated with the equilibrium constants proposed by Östholts *et al.* [1994OST/BRU] for $\text{Th}(\text{OH})_4(\text{aq})$ and $\text{Th}(\text{OH})_3(\text{CO}_3)^-$ (see text for notation of Th(IV) hydroxide-carbonate complexes).



XI.1.3.2.1.2 Solubility studies in carbonate/bicarbonate buffers

Östhols *et al.* [1994OST/BRU] and Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC] also measured the solubility of ThO₂(am, hyd) in carbonate/bicarbonate buffers of constant ionic strength and given total carbonate concentration ($C_{\text{tot}} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$). In [2005ALT/NEC] the pH range was extended up to pH 13 by adding NaOH. The solubility data at $I = 0.5$ M (NaHCO₃-Na₂CO₃-NaClO₄ solutions with $C_{\text{tot}} = 0.1$ M [1994OST/BRU] and NaHCO₃-Na₂CO₃-NaOH-NaCl solutions with $C_{\text{tot}} = 0.1, 0.04$ and 0.015 M [2005ALT/NEC]) were also included in the data evaluation of [2005ALT/NEC]. As shown in Figure XI-3 for the highest and lowest values of $C_{\text{tot}} = 0.1$ and 0.015 M at $I = 0.5$ M, the complex (114) = Th(OH)(CO₃)₄⁵⁻ is the dominant species at pH 8–10.5 and responsible for the relatively high solubility in this pH range. The complex (141) = Th(OH)₄(CO₃)₂²⁻, dominant at pH > 11, causes only a slight increase of the solubility compared to carbonate-free solutions.

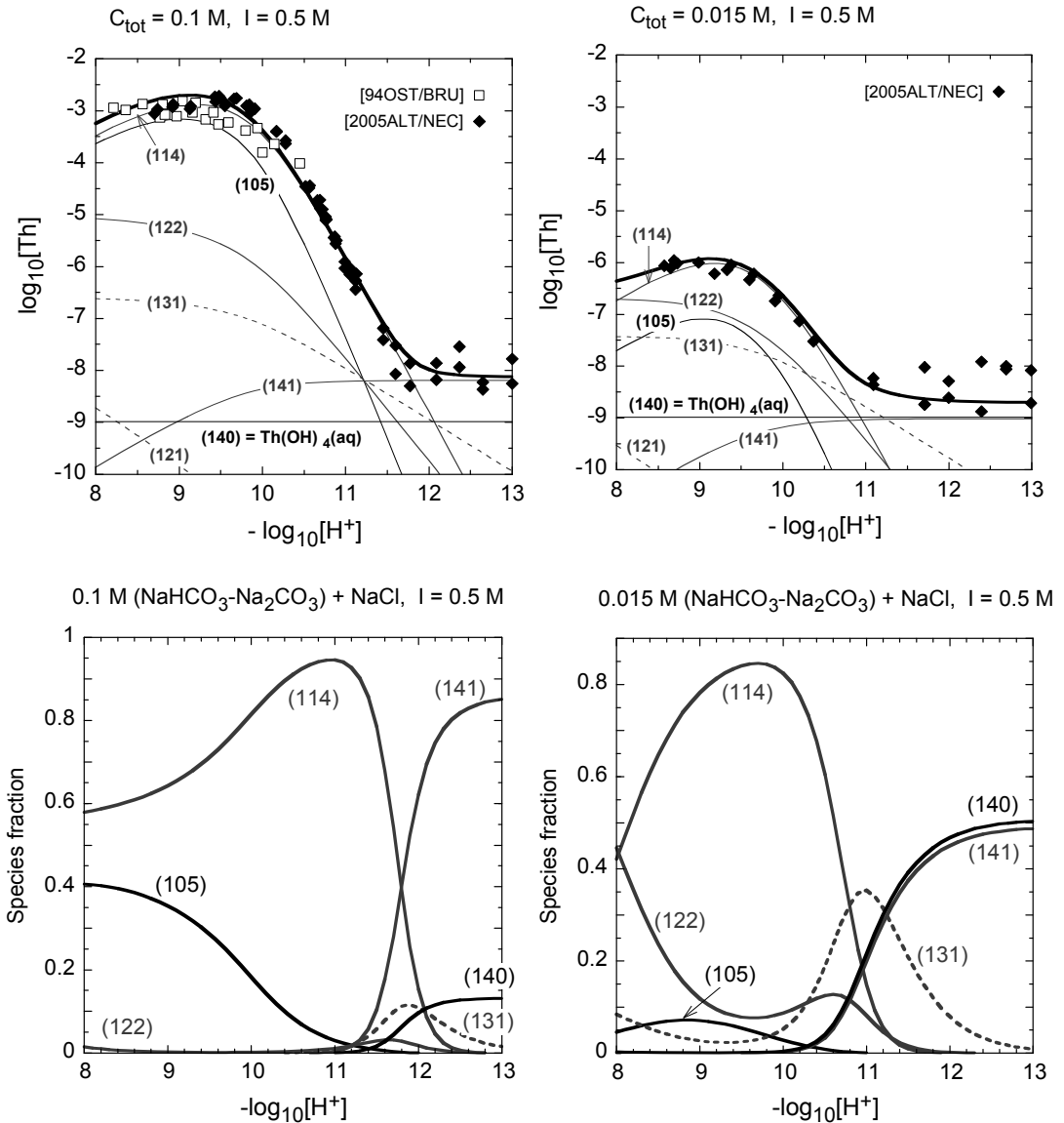
In their most recent study, Altmaier *et al.* [2006ALT/NEC] extended their solubility study with ThO₂(am, hyd) to cover a wider range of ionic strength. As shown in Appendix A, the experimental solubility data at a total carbonate concentration of $C_{\text{tot}} = 0.02$ M and constant ionic strengths of $I = 0.1, 0.5, 2.0$ and 4.0 M (NaHCO₃-Na₂CO₃-NaCl) are well predicted with the equilibrium constants and SIT coefficients selected by this review. The large increase of the solubility in the range of the maximum at $-\log_{10}[\text{H}^+]$ around 9.5, from $\log_{10}[\text{Th}] = -6.2$ at $I = 0.1$ M to -3.4 at $I = 4.0$ M, is consistent with the ionic strength dependence expected for the reaction:



The same holds for the solubility increase of about an order of magnitude at $C_{\text{tot}} = 0.1$ M, when the ionic strength is kept constant at $I = 0.5$ M by adding NaCl or NaClO₄ compared to that in 0.1 M (NaHCO₃-Na₂CO₃) without addition of background electrolyte, *i.e.*, at the same carbonate concentration but at somewhat lower (variable) ionic strength of $I = [\text{HCO}_3^-] + 3[\text{CO}_3^{2-}] = 0.1$ M at $-\log_{10}[\text{H}^+] < 9$ and 0.3 M at $-(\log_{10}[\text{H}^+] > 10)$.

The (105) complex Th(CO₃)₅⁶⁻ was not included in the model calculations of Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC] but the equilibrium constant selected by this review for the pentacarbonate complex (Section XI.1.3.2.2) does not lead to a significant change of the calculated solubility under the conditions of the test solutions (carbonate/bicarbonate buffers at $-\log_{10}[\text{H}^+] = 8-13$ and $C_{\text{tot}} \leq 0.1$ M, $-\log_{10}[\text{H}^+] = 5.0-7.6$ under 0.1 bar CO₂(g) and $-\log_{10}[\text{H}^+] = 4.4-6.6$ under 1.0 bar CO₂(g)) if used in addition to their data for the ternary complexes (*cf.* Figure XI-2 and Figure XI-3). The pentacarbonate complex is not dominant under these conditions; however, as shown in Figure XI-2, it is calculated to be the dominant species at $-\log_{10}[\text{H}^+] > 7.6$ under 0.1 bar CO₂(g) and at $-\log_{10}[\text{H}^+] > 6.6$ under 1.0 bar CO₂(g).

Figure XI-3: Solubility of $\text{ThO}_2(\text{am, hyd})$ and speciation at $I = 0.5 \text{ M}$ ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaOH-NaCl}$) and a total carbonate concentration of $C_{\text{tot}} = 0.1$ and 0.015 M [2005ALT/NEC]. The corresponding data of [1994OST/BRU] at $C_{\text{tot}} = 0.1$ and $I = 0.5 \text{ M}$ (NaClO_4 media) are shown for comparison. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and $\log_{10} K_{s,0}^\circ = -(47.6 \pm 0.5)$ calculated from the data in carbonate-free solutions.



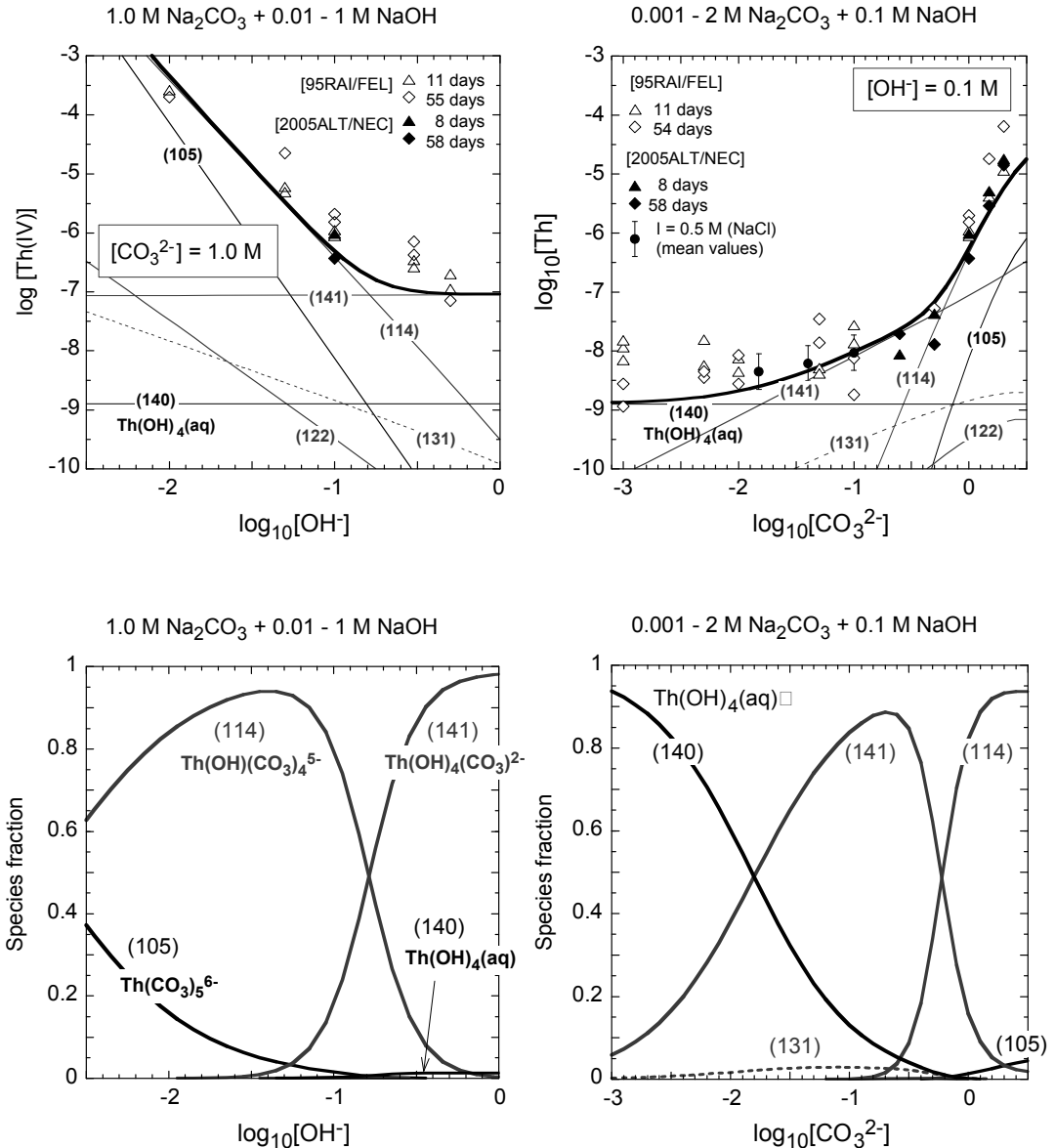
The solubility determined by Rai *et al.* [1995RAI/FEL], [1997FEL/RAI] with ThO₂(am, hyd) in 0.01–0.25 M NaHCO₃ solutions of varying ionic strength is also well described with the equilibrium constants and SIT coefficients selected by this review (*cf.* Appendix A). The complex (122) = Th(OH)₂(CO₃)₂²⁻ is calculated to be dominant in 0.01–0.05 M NaHCO₃. This is consistent with the models proposed by Rai *et al.* for U(IV) [1998RAI/FEL], Np(IV) [1999RAI/HES] and Pu(IV) [1999RAI/HES2]. The complex (114) = Th(OH)(CO₃)₄⁵⁻ is dominant in 0.05–0.4 M NaHCO₃ and, as confirmed by EXAFS measurements [1997FEL/RAI], the pentacarbonate complex (105) = Th(CO₃)₅⁶⁻ is dominant in bicarbonate solutions above 0.4 M.

XI.1.3.2.1.3 Solubility studies at high pH and carbonate concentration

Solubility data determined by Rai *et al.* [1995RAI/FEL], [1997FEL/RAI] with ThO₂(am, hyd) in 1.0 M Na₂CO₃ containing 0.01–1.0 M NaOH and in 0.001–2.0 M Na₂CO₃ containing 0.1 M NaOH were confirmed by some additional experimental data of [2005ALT/NEC]. Although these conditions partly exceed the validity range of the SIT, the solubilities predicted with the equilibrium constants and SIT coefficients selected in the present review are in good agreement with the experimental data (Figure XI-4). The dependence of the solubility on log₁₀[OH⁻] and log₁₀[CO₃²⁻] is reasonably consistent with the dominance of the complexes (141) = Th(OH)₄(CO₃)₂²⁻ and (114) = Th(OH)(CO₃)₄⁵⁻, but not with the limiting carbonate complex (105) = Th(CO₃)₅⁶⁻.

Altmaier *et al.* [2005ALT/NEC] noticed that a somewhat better fit is obtained by including (in addition to the species given in Table XI-3) the complex Th(OH)₂(CO₃)₄⁶⁻ with log₁₀ β₁₂₄^o ≤ (34.3 ± 0.6) and an estimated interaction coefficient of ε(Th(OH)₂(CO₃)₄⁶⁻, Na⁺) = -(0.3 ± 0.2) kg·mol⁻¹. This holds as well for two further sets of experimental data from [1999FEL/RAI] in 2.33 and 4.67 m NaCl containing 0.1–2.3 M Na₂CO₃ and 0.1 M NaOH, in particular for the higher carbonate concentrations in 4.67 m NaCl (*cf.* Appendix A review of [1999FEL/RAI]). However, these conditions are beyond the validity range of the SIT and changing ε(Th(OH)(CO₃)₄⁵⁻, Na⁺) or ε(Th(CO₃)₅⁶⁻, Na⁺) within their uncertainty ranges also yields good fits. Felmy *et al.* [1999FEL/RAI] described their results with Pitzer's ion interaction approach including binary and ternary parameters for the complex Th(CO₃)₅⁶⁻ given in Appendix A.

Figure XI-4: Solubility of $\text{ThO}_2(\text{am, hyd})$ and speciation at high pH and carbonate concentration: Experimental data from [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC] in 1.0 M Na_2CO_3 containing 0.01–1.0 M NaOH (left side) and in 0.001–2.0 M Na_2CO_3 containing 0.1 M NaOH (right side). The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K_{s,0}^\circ$ (aged $\text{ThO}_2(\text{am, hyd})$) = -47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.



XI.1.3.2.1.4 Summary

The available solubility data for ThO₂(am, hyd) in carbonate solution (19 sets of experimental data from different groups of authors) under widely varying conditions: pH 4.5–13, carbonate concentrations up to 2 M and ionic strength varying from $I = 0.1$ M to 4.0 M (even up more than 6 M) are well described with only a few ternary complexes, the most important ones being Th(OH)(CO₃)₄⁵⁻, Th(OH)₂(CO₃)₂²⁻ and Th(OH)₄(CO₃)₂²⁻.

The (114) complex (Th(OH)(CO₃)₄⁵⁻) is responsible for the high Th concentrations in the solubility studies with ThO₂(am, hyd) at pH 7–8 under 0.1–1.0 bar CO₂(g) (Figure XI-2) and at pH 8–10 at $C_{\text{tot}} = 0.02–0.1$ M (Figure XI-3), in particular at high ionic strength, but also at high pH (pH 11–13) and carbonate concentrations of 0.3–2.0 M (Figure XI-4).

The (122) complex (Th(OH)(CO₃)₄⁵⁻) is dominant both at pH 5.5–7 under 0.1–1.0 bar CO₂(g) (Figure XI-2) and at $C_{\text{tot}} = 0.01–0.1$ and pH 8–9, particularly at low ionic strength (*e.g.*, in bicarbonate solutions as also shown in analogous solubility studies with U(IV), Np(IV) and Pu(IV) hydrous oxides [1998RAI/FEL], [1999RAI/HES], [1999RAI/HES2]). The contribution of this complex to the thorium concentration in solubility studies with ThO₂(am, hyd) is in the range $10^{-7}–10^{-4}$ M.

The (141) complex (Th(OH)(CO₃)₄⁵⁻) is the dominant species at pH > 11 and carbonate concentrations in the range of 0.02–0.5 M (Figure XI-3 and Figure XI-4). The concentration of this complex is rather low and does not exceed 2×10^{-7} M. However, its concentration is significantly greater than that of Th(OH)₄(aq).

Hence, the following formation constants and SIT coefficients are selected:

$$\log_{10} \beta_{114}^{\circ} (\text{Th(OH)(CO}_3)_4^{5-}, 298.15 \text{ K}) = (35.6 \pm 0.5)$$

$$\varepsilon (\text{Th(OH)(CO}_3)_4^{5-}, \text{Na}^+) = -(0.22 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}.$$

$$\log_{10} \beta_{112}^{\circ} (\text{Th(OH)}_2(\text{CO}_3)_2^{2-}, 298.15 \text{ K}) = (36.8 \pm 0.5)$$

$$\varepsilon (\text{Th(OH)}_2(\text{CO}_3)_2^{2-}, \text{Na}^+) = -(0.1 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}.$$

$$\log_{10} \beta_{141}^{\circ} (\text{Th(OH)}_4(\text{CO}_3)_2^{2-}, 298.15 \text{ K}) = (40.4 \pm 0.6)$$

$$\varepsilon (\text{Th(OH)}_4(\text{CO}_3)_2^{2-}, \text{Na}^+) = -(0.1 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}.$$

The complexes Th(OH)₂(CO₃)(aq) and Th(OH)₃(CO₃)⁻ are found to be relevant only at low carbonate concentrations in the near neutral pH range, *e.g.*, in the studies under 0.1 and 1.0 bar CO₂(g) they have maximum contributions of 30–50 % in the solubility minimum range at pH 5–6 (Figure XI-2). The speciation schemes indicate that the predominance regions of Th(OH)₂(CO₃)(aq) and Th(OH)₃(CO₃)⁻ are between those of Th(OH)₂²⁺, Th(OH)₂(CO₃)₂²⁻ and Th(OH)₄(aq). However, the maximum effect on the calculated solubility is less than 0.3 log₁₀-units (at thorium concentrations of $10^{-8}–10^{-6}$ M). Under nearly all other conditions these two species are

negligible. The formation constants and SIT coefficients

$$\log_{10} \beta_{121}^{\circ} (\text{Th}(\text{OH})_2(\text{CO}_3)(\text{aq}), 298.15 \text{ K}) = (30.5 \pm 0.6)$$

(SIT coefficients equal to zero)

$$\log_{10} \beta_{131}^{\circ} (\text{Th}(\text{OH})_3(\text{CO}_3)^-, 298.15 \text{ K}) = (38.3 \pm 0.7)$$

$$\varepsilon(\text{Th}(\text{OH})_3(\text{CO}_3)^-, \text{Na}^+) = -(0.05 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}.$$

are not selected but recommended as guidance. The speciation lines of these complexes are shown as dashed lines in the model calculations.

The solubility data at high carbonate concentrations ($> 0.5 \text{ M}$) and $\text{pH} > 12$ [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], in particular with additions of NaCl, can be better described by assuming the formation of an additional (124) complex = $\text{Th}(\text{OH})_2(\text{CO}_3)_4^{6-}$, with:

$$\log_{10} \beta_{124}^{\circ} (\text{Th}(\text{OH})_2(\text{CO}_3)_4^{6-}, 298.15 \text{ K}) \leq (34.3 \pm 0.6)$$

$$\varepsilon(\text{Th}(\text{OH})_2(\text{CO}_3)_4^{6-}, \text{Na}^+) = -(0.3 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}.$$

(A similar situation occurred in the evaluation of the U(IV) solubility data in 3.0 and 3.3 m K_2CO_3 containing 0.01–0.8 m NaOH or KOH, respectively, *cf.*, Appendix A review of [1998RAI/FEL] in [2003GUI/FAN]). However, these conditions are beyond the validity range of the SIT. Moreover, the model is not unique; changing $\varepsilon(\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}, \text{Na}^+)$ or $\varepsilon(\text{Th}(\text{CO}_3)_5^{6-}, \text{Na}^+)$ within their uncertainty ranges also yields good fits. Under all other conditions discussed in this review this complex is a minor species (less than 10%). Therefore an equilibrium constant for this complex was not selected.

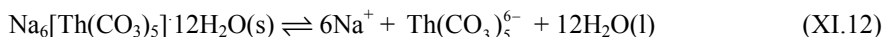
XI.1.3.2.2 Formation constant of $\text{Th}(\text{CO}_3)_5^{6-}$

The pentacarbonate complex (105) is not dominant in the studies discussed above, but is in carbonate and bicarbonate solutions at $C_{\text{tot}} > 0.2 \text{ M}$ and $\text{pH} = 8-11$ (*e.g.*, in 0.2–2 M NaHCO_3 or Na_2CO_3 , see below) where the solubility of $\text{ThO}_2(\text{am, hyd})$ is very high. Additional studies based on solubility experiments of Östhols *et al.* [1994OST/BRU], Altmaier *et al.* [2006ALT/NEC] and Felmy *et al.* [1997FEL/RAI], liquid-liquid extraction by João *et al.* [1987JOA/BIG2], [1995JOA/BUR] and EXAFS data [1997FEL/RAI], [2006ALT/NEC] will be discussed in this section.

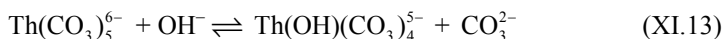
The limiting carbonate complex is an important species in the Th(IV)-carbonate system. However, as discussed above, the formation constant of $\text{Th}(\text{CO}_3)_5^{6-}$ is not available directly from the solubility measurements in [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC], [2006ALT/NEC]. All solubility measurements with $\text{ThO}_2(\text{am, hyd})$ were performed either at carbonate concentrations $C_{\text{tot}} \leq 0.1 \text{ M}$, which is not high enough to form $\text{Th}(\text{CO}_3)_5^{6-}$ as the dominant complex, or at $\text{pH} > 12$ where, due to the competition between OH^- and CO_3^{2-} ligands, ternary complexes $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ and possibly $\text{Th}(\text{OH})_2(\text{CO}_3)_4^{6-}$ become dominant, even at high

carbonate concentrations.

In the intermediate range, $0.2 \text{ M} < C_{\text{tot}} < 2 \text{ M}$ and $\text{pH} = 8 - 11$ (e.g., in $0.2 - 2 \text{ M}$ NaHCO_3 or Na_2CO_3 solutions), where EXAFS studies have identified the limiting carbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$ as the dominant species, the solubility of $\text{ThO}_2(\text{am, hyd})$ is very high. Under these conditions the solubility of thorium is limited by $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ with thorium concentrations in the range $0.02 - 0.05 \text{ M}$ [1961LUZ/KOV2], [1973DER/FAU3]. There is no other independent thermodynamic information for this solid phase; therefore only the equilibrium constant for the reaction:



can be derived (*cf.*, Section XI.1.3.3), but not the formation constant $\log_{10} \beta_{105}^\circ$. It may seem surprising that the limiting carbonate complex $\text{Th}(\text{CO}_3)_5^{6-}$ is also dominant in NaHCO_3 solutions above 0.2 M where the concentration of CO_3^{2-} is orders of magnitude lower than in the corresponding Na_2CO_3 solutions. However, the same holds true for the competing OH^- ligand and the ratio between the two most important complexes $[\text{Th}(\text{CO}_3)_5^{6-}] : [\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}]$ under these conditions does not depend on the absolute concentration of carbonate but on the ratio $[\text{CO}_3^{2-}] / [\text{OH}^-]$ according to:



with

$$\log_{10} \frac{[\text{Th}(\text{CO}_3)_5^{6-}]}{[\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}]} = \log_{10} \beta_{105} - \log_{10} \beta_{114} + \log_{10} \frac{[\text{CO}_3^{2-}]}{[\text{OH}^-]} \quad (\text{XI.14})$$

The equilibrium constants derived from the solvent extraction studies of Joao *et al.* [1987JOA/BIG2], [1995JOA/BUR] are not reliable. For instance with $\log_{10} \beta_{105} = (28.3 \pm 0.2)$ derived from the study of [1987JOA/BIG2] at $I = 1.0 \text{ M}$ (guanidinium carbonate / bicarbonate solution) and assuming the same value for $I = 1.0 \text{ M}$ (Na_2CO_3 - NaHCO_3), the concentration of $\text{Th}(\text{CO}_3)_5^{6-}$ is always significantly below that of $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ ($\log_{10} \beta_{114} = (34.2 \pm 0.5)$ at $I = 1.0 \text{ M}$). The ratio between the two complexes is given by:

$$\log_{10} \frac{[\text{Th}(\text{CO}_3)_5^{6-}]}{[\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}]} = -(5.9 \pm 0.5) + \log_{10} \frac{[\text{CO}_3^{2-}]}{[\text{OH}^-]} \quad (\text{XI.15})$$

where $\log_{10} \frac{[\text{CO}_3^{2-}]}{[\text{OH}^-]}$ is generally smaller than 5.

The solubility data determined with a dried Th(IV) oxyhydroxide phase at $I = 0.5 \text{ M}$, both at $C_{\text{tot}} = 0.1 \text{ M}$ and under CO_2 partial pressures of 1.0 and 0.1 bar [1994OST/BRU], [2005ALT/NEC], set an upper limit for the formation constant of $\text{Th}(\text{CO}_3)_5^{6-}$. Altmaier *et al.* [2005ALT/NEC] indicate that $\log_{10} K_{s,105}^\circ$ is more negative than -16.6 , which is consistent, within the uncertainties, with the value of $-(16.4 \pm 0.3)$ from [1994OST/BRU]. If this value is combined with $\log_{10} K_{s,0}^\circ = -(47.6 \pm 0.5)$ or

– (48.0 ± 0.5) , respectively (calculated by this review from the solubility data determined in these studies with the same solid phase in carbonate-free solutions), an upper limit of $\log_{10} \beta_{105}^{\circ} < (31.3 \pm 0.6)$ is obtained.

EXAFS measurements in various carbonate and bicarbonate solutions [1997FEL/RAI], [1997HES/FEL], [2006ALT/NEC] give only qualitative information on the speciation because the spectra could not be deconvoluted into single component contributions. However, in combination with the known formation constant of $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ ($\log_{10} \beta_{114}^{\circ} = (35.6 \pm 0.5)$, *cf.* Section XI.1.3.2.1), the most important competing species in these solutions, the information from the EXAFS studies allows the estimation of the equilibrium constant $\log_{10} \beta_{105}^{\circ}$ within a certain range.

Felmy *et al.* [1997FEL/RAI], [1997HES/FEL] recorded EXAFS spectra of Th(IV) in 1.0 or 2.0 M Na_2CO_3 ¹ and in 1.0, 0.5, 0.25, 0.17, and 0.10 M NaHCO_3 . In the Na_2CO_3 solution and in 1.0 and 0.5 M NaHCO_3 the limiting carbonate complex is undoubtedly the dominant species. In the 0.25 and 0.17 M NaHCO_3 solutions the average number of CO_3^{2-} ligands (derived from the Th-C and Th- O_{distal} scattering paths) decreases slightly. The distance $r(\text{Th-O})$ and the total coordination number ($N_{\text{O}} = (10 \pm 1)$) remain approximately constant, whereas in 0.10 M NaHCO_3 both $r(\text{Th-O})$ and N_{O} and also the number of CO_3^{2-} ligands is significantly lower. As particularly the coordination numbers have large uncertainties, a quantitative speciation or a clear-cut identification of the complexes is not possible. However, applying Equation (XI.14) a minimum value for the formation constant of $\text{Th}(\text{CO}_3)_5^{6-}$ can be derived from the observation that $\text{Th}(\text{CO}_3)_5^{6-}$ is the major complex at NaHCO_3 concentrations above 0.3 M. The pH of these solutions is not given in [1997FEL/RAI], but in comparable samples of U(IV) [1998RAI/FEL] and Pu(IV) [1999RAI/HES2] in 0.2–0.5 M bicarbonate solution the H^+ concentration is in the range $-\log_{10} [\text{H}^+] = 8-9$. Using NEA-TDB auxiliary data to calculate the dissociation constant of water and the protonation constant of carbonate in 0.3 M NaHCO_3 at $-\log_{10} [\text{H}^+] = 8-9$, we obtain an approximately constant value of $\log_{10}([\text{CO}_3^{2-}]/[\text{OH}^-]) = 3.5$. Combining this value with $\log_{10} \beta_{114}^{\circ} = (34.4 \pm 0.5)$ ($\log_{10} \beta_{114}^{\circ} = (35.6 \pm 0.5)$), the relation $[105]/[114] > 1$ (more than 50% of the thorium present as $\text{Th}(\text{CO}_3)_5^{6-}$) requires a minimum value of $\log_{10} \beta_{105}^{\circ} > (30.9 \pm 0.5)$. Extrapolation to zero ionic strength with the SIT yields the following lower limit: $\log_{10} \beta_{105}^{\circ} > (30.8 \pm 0.5)$.

Altmaier *et al.* [2006ALT/NEC] reported an EXAFS spectrum of a thorium solution in 1.0 M $\text{Na}_2\text{CO}_3/0.1$ M NaHCO_3 which is consistent with those measured in [1997FEL/RAI] for thorium solutions at high carbonate or bicarbonate concentrations. However, the EXAFS spectrum of a saturated solution taken from the solubility study at $I = 0.5$ M ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaCl}$), $C_{\text{tot}} = 0.1$ M, and $-\log_{10} [\text{H}^+] = 9.16$ ($\log_{10}([\text{CO}_3^{2-}]/[\text{OH}^-]) = 3.0$) is clearly different and indicates that the limiting carbon-

¹ The exact composition of this solution is not known, *cf.* Appendix A review of [1997FEL/RAI].

ate complex is not dominant (less than 50%) under these conditions [2006ALT/NEC]. As $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ (with $\log_{10} \beta_{114} = (34.3 \pm 0.5)$, $\log_{10} \beta_{114}^\circ = (35.6 \pm 0.5)$) is the only other relevant species in this solution, the relation $[\text{105}]/[\text{114}] < 1$ yields an upper limit of $\log_{10} \beta_{105} < (31.3 \pm 0.5)$ (corresponding to $\log_{10} \beta_{105}^\circ < (31.2 \pm 0.5)$). This observation is consistent with the interpretation of the solubility data under these conditions [2005ALT/NEC], [2006ALT/NEC] (*cf.* Figure XI-3 in Section XI.1.3.2.1).

Table XI-5: Equilibrium constants for $\text{Th}(\text{CO}_3)_5^{6-}$ at 22–25°C (uncertainties are given as 2σ).

Method	$\log_{10} K_{s,105}^\circ$	$\log_{10} \beta_{105}^\circ$	Reference
extr		28.3 ± 0.2^a	[1987JOA/BIG2]
extr		21.5 ± 0.5^b	[1995JOA/BUR]
sol	< -16.6	$< 31.0 \pm 0.5^c$	[2005ALT/NEC]
sol	-16.4 ± 0.4	31.6 ± 0.6^c	[1994OST/BRU]
sol	-18.4^d	29.1 ± 0.9^c	[1997FEL/RAI]
		31.0 ± 0.7	This review

- a: $\log_{10} \beta_{105}$ at $I = 1.0$ M (guanidinium carbonate/bicarbonate solution), recalculated by this review, *cf.* Appendix A.
- b: This value is the average from experimental data at three different ionic strengths, 0.025, 0.050 and 0.70 M extrapolated to $I = 0$ by this review using $\Delta\epsilon = -0.6 \text{ kg}\cdot\text{mol}^{-1}$, based on the interaction coefficients in Appendix B and assuming $\epsilon(\text{Th}(\text{CO}_3)_5^{6-}, \text{NH}_4^+/\text{C}(\text{NH}_2)_3^+) = \epsilon(\text{U}(\text{CO}_3)_5^{6-}, \text{Na}^+)$ in the ammonium/guanidinium nitrate medium used. For reasons given in Appendix A, these values have not been accepted by this review.
- c: Calculated according to: $\log_{10} \beta_{105}^\circ = \log_{10} K_{s,105}^\circ - \log_{10} K_{s,0}^\circ$ with the $\log_{10} K_{s,0}^\circ$ values calculated by this review: $\log_{10} K_{s,0}^\circ = -(47.6 \pm 0.5)$ [2005ALT/NEC], $-(48.0 \pm 0.5)$ [1994OST/BRU], or $-(47.5 \pm 0.9)$ selected for aged $\text{ThO}_2(\text{am, hyd})$.
- d: Based on Pitzer's ion interaction approach (*cf.* Appendix A review of [1997FEL/RAI]) and hence not directly comparable to the $\log_{10} K_{s,105}^\circ$ values from [1994OST/BRU] and [2005ALT/NEC] which are calculated with the SIT.

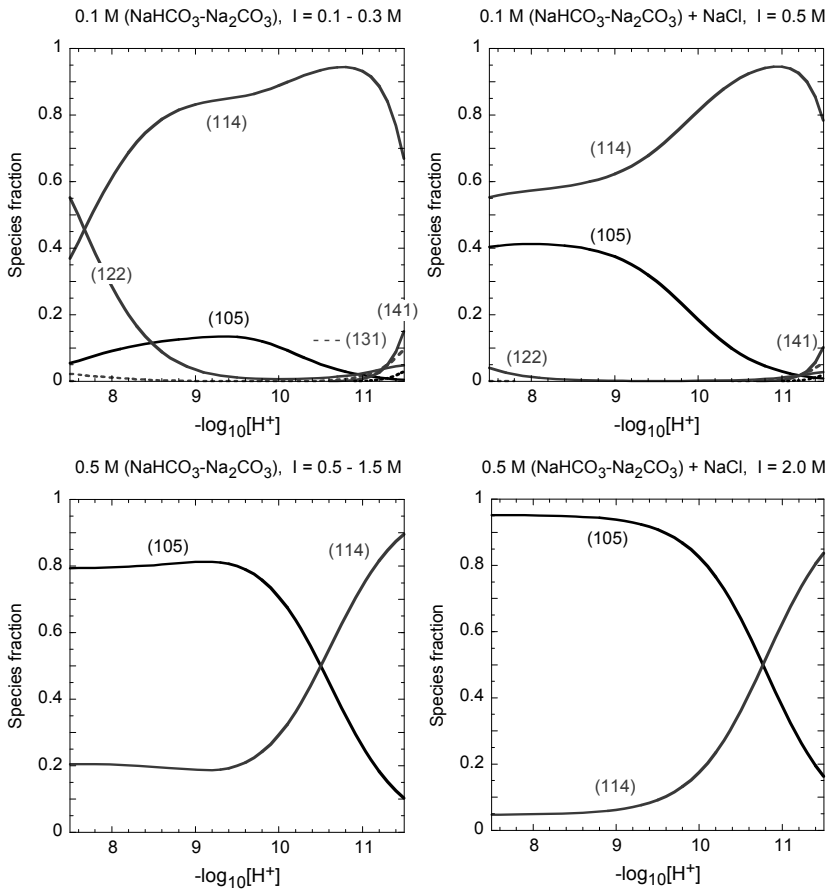
Combining the information from the solubility of $\text{ThO}_2(\text{am, hyd})$ at $I = 0.5$ M [1994OST/BRU], [2005ALT/NEC] and from the EXAFS studies in carbonate and bicarbonate solutions [1997FEL/RAI], [2006ALT/NEC], the formation constant of $\text{Th}(\text{CO}_3)_5^{6-}$ must be in the range: $(30.8 \pm 0.5) < \log_{10} \beta_{105}^\circ < (31.2 \pm 0.5)$. Based on the ion interaction coefficient $\epsilon(\text{Th}(\text{CO}_3)_5^{6-}, \text{Na}^+) = \epsilon(\text{U}(\text{CO}_3)_5^{6-}, \text{Na}^+) = -(0.30 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$, this review selects a value of:

$$\log_{10} \beta_{105}^\circ (\text{Th}(\text{CO}_3)_5^{6-}, 298.15 \text{ K}) = (31.0 \pm 0.7)$$

where the uncertainty covers the whole range of values deduced from the previous discussions. In order to illustrate the discussion above, Figure XI-5 shows speciation

schemes calculated with the selected formation constants for $\text{Th}(\text{CO}_3)_5^{6-}$ and the ternary $\text{Th}(\text{IV})$ -hydroxide-carbonate complexes.

Figure XI-5: Speciation schemes calculated with the selected formation constants for $\text{Th}(\text{CO}_3)_5^{6-}$ and the ternary $\text{Th}(\text{IV})$ -hydroxide-carbonate complexes. Left side: 0.1 and 0.5 M NaHCO_3 - Na_2CO_3 solutions of varying ionic strength ($I = [\text{NaHCO}_3] + 3[\text{Na}_2\text{CO}_3]$)¹. Right side: NaHCO_3 - Na_2CO_3 - NaCl (or NaClO_4) solutions of the same carbonate concentration ($C_{\text{tot}} = 0.1$ and 0.5 M), but at constant ionic strength ($I = 0.5$ and 2.0 M, respectively.)

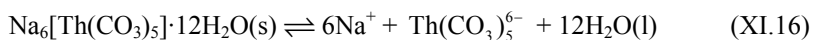


¹ The calculations are accounting for the continuous variation of $\log_{10} K_w$, $\log_{10} K_2$ (protonation constant of CO_3^{2-}) and the formation constants of the thorium complexes when ionic strength varies from $I = m_{\text{NaHCO}_3}$ at $\text{pH} < 9$ to $I = 3 m_{\text{Na}_2\text{CO}_3}$ at $\text{pH} > 10$.

The speciation depends not only on the H^+ and carbonate concentration; it is also significantly affected by the ionic strength. Higher ionic strength favours the formation of the higher charged complex $Th(CO_3)_5^{6-}$ ($z^2 = 36$) compared to $Th(OH)(CO_3)_4^{5-}$ ($z^2 = 25$) and particularly compared to $Th(OH)_2(CO_3)_2^{2-}$ ($z^2 = 4$) (*cf.* the speciation at $C_{tot} = 0.1$ M in pure $NaHCO_3$ - Na_2CO_3 solution ($I = 0.1-0.3$ M, left side) and in $NaHCO_3$ - Na_2CO_3 -($NaCl$ or $NaClO_4$) with ionic strength kept constant at $I = 0.5$ M by additions of $NaCl$ or $NaClO_4$ (right side).

XI.1.3.3 Solubility of $Na_6[Th(CO_3)_5] \cdot 12H_2O(s)$ and $[C(NH_2)_3]_6[Th(CO_3)_5] \cdot 4H_2O(s)$

There are two experimental studies of the solubility of $Na_6[Th(CO_3)_5] \cdot 12H_2O(s)$ in sodium carbonate and bicarbonate solutions, from Luzhnaya and Kovaleva [1961LUZ/KOV2] and Dervin and Faucherre [1973DER/FAU3]. These studies are discussed in Appendix A. This review has reinterpreted the experimental data and calculated the solubility product $\log_{10} K_{s,5}^{\circ}$ for the reaction:



The values of $\log_{10} K_{s,5}^{\circ} = -(11.3 \pm 0.3)$, $-(11.2 \pm 0.4)$, and $-(11.0 \pm 0.5)$ derived by this review from the solubility of $Na_6[Th(CO_3)_5] \cdot 12H_2O(s)$ in $0.79-2.8$ m Na_2CO_3 [1961LUZ/KOV2], in Na_2CO_3 - $NaNO_3$ solution (at $[Na^+] = 2.0$ M and $[CO_3^{2-}] = 0.15-1.0$ M) [1973DER/FAU3], and in 2.0 M $NaHCO_3$ - $NaNO_3$ (at $[Na^+] = 2.0$ M and $[HCO_3^-] = 0.2-1.0$ M) [1973DER/FAU3], respectively, are in good agreement, in particular taking into account the relatively large uncertainties arising from the SIT coefficients used for the extrapolation to zero ionic strength. However it should be noted that the values at zero ionic strength are only based on the experimental data at $I < 5$ mol·kg⁻¹. The following mean value is selected:

$$\log_{10} K_{s,5}^{\circ}(Na_6[Th(CO_3)_5] \cdot 12H_2O(s)) = -(11.2 \pm 0.4).$$

It is not possible to calculate the formation constant of $Th(CO_3)_5^{6-}$ from these data; however, they provide information of the stoichiometry of the dominant complex.

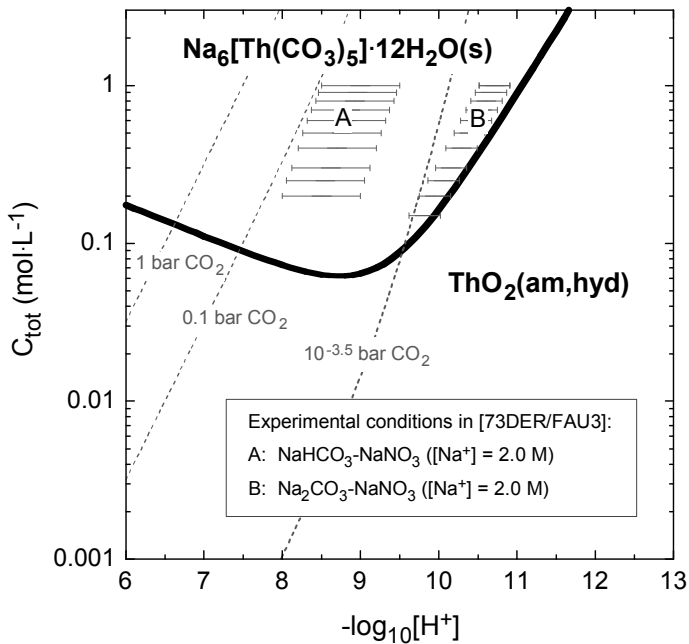
Figure XI-6 shows the stability field of $Na_6[Th(CO_3)_5] \cdot 12H_2O(s)$ compared to $ThO_2(am, hyd)$, which is found to be the stable solubility limiting phase in many other solubility studies [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC], [2006ALT/NEC]. These solubility measurements with $ThO_2(am, hyd)$ were performed either at carbonate concentrations $C_{tot} \leq 0.1$ M or at $pH > 12$. The borderline for the solid transformation:



is calculated for the conditions in [1973DER/FAU3] ($NaHCO_3$ - Na_2CO_3 - $NaNO_3$ solutions at a constant sodium ion concentration of $[Na^+] = 2.0$ M). $Na_6[Th(CO_3)_5] \cdot 12H_2O(s)$ is stable only at high Na^+ and carbonate concentrations but Figure XI-6 shows that it is not stable at high pH, where $ThO_2(am, hyd)$ is the stable phase. The stability region of $Na_6[Th(CO_3)_5] \cdot 12H_2O(s)$ coincides with the range where

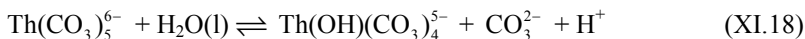
the solubility of $\text{ThO}_2(\text{am, hyd})$ is rather high ($[\text{Th}]_{\text{tot}} > 0.01 \text{ M}$) and with the range where $\text{Th}(\text{CO}_3)_5^{6-}$ is the dominant complex in solution.

Figure XI-6: Stability region of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ compared to aged $\text{ThO}_2(\text{am, hyd})$ ($\log_{10} K_{s,0}^\circ = -47.5$) at $[\text{Na}^+] = 2.0 \text{ M}$ ($\text{NaHCO}_3\text{-Na}_2\text{CO}_3\text{-NaNO}_3$) and 25°C . The regions A and B indicate the experimental conditions in [1973DER/FAU3]; the dotted lines show the corresponding values of the total carbonate concentration C_{tot} and $-\log_{10}[\text{H}^+]$ for equilibrium CO_2 partial pressures of 1.0, 0.1, and $10^{-3.5}$ bar (air).



The approximately constant solubility of 0.021 to 0.029 mol·L⁻¹ observed by [1973DER/FAU3] for all bicarbonate and most of the carbonate solutions (up to 0.5 M Na_2CO_3) indicates that ternary Th(IV)-hydroxide-carbonate complexes are not dominant under these conditions. The formation of additional complexes would increase the solubility significantly. A test as to whether the thermodynamic data selected in this review, in particular for the complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$, are compatible with the experimental data of [1973DER/FAU3] requires the values of pH or H^+ concentration which were not determined by [1973DER/FAU3]. The following section describes an alternative method of testing the compatibility.

The pH values in the bicarbonate solutions are estimated ([1998RAI/FEL], [1999RAI/HES2]) to be in the range of 8–9.5 for 0.2–1.0 M bicarbonate solutions and they clearly fall in the stability region of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ (*cf.* region A in Figure XI-6). For the Na_2CO_3 - NaNO_3 solutions in [1973DER/FAU3] the situation is more complicated. Assuming a closed system, the H^+ concentrations of the NaNO_3 solutions containing 0.2–1.0 M Na_2CO_3 are calculated to be in the range $-\log_{10}[\text{H}^+] = 11.0$ – 11.5 which is outside the stability range of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$. However, the precipitation of $\text{ThO}_2(\text{am, hyd})$ with a much lower solubility under these conditions (*cf.* Figure XI-7 and Figure XI-8 below) was not observed by [1973DER/FAU3]. Moreover, $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ is calculated to be the dominant complex at these pH values and hence the solubility of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ would be considerably increased by the formation of this additional complex, but this was not observed by [1973DER/FAU3] (maximum solubility in 1.0 M Na_2CO_3 : $[\text{Th}]_{\text{tot}} = 0.046 \text{ mol} \cdot \text{L}^{-1}$). On the other hand, the formation of $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ according to:



results in a decrease of pH. For instance in 1.0 M Na_2CO_3 , an equilibrium state would be reached at $-\log_{10}[\text{H}^+] = 10.9$ for a solution containing 0.025 M $\text{Th}(\text{CO}_3)_5^{6-}$ and 0.021 M $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$. A further decrease of pH, particularly for the lower carbonate concentrations, is expected due to the absorption of $\text{CO}_2(\text{g})$ from the atmosphere. Therefore we may estimate that the pH values are a) in the stability field of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ and b) shifted to the values in equilibrium with the CO_2 partial pressure of air (*cf.* region B in Figure XI-6).

Figure XI-7 and Figure XI-8 show the solubility data of Dervin and Faucherre [1973DER/FAU3] at the highest and the lowest total carbonate concentration of $C_{\text{tot}} = 1.0$ and 0.2 M, respectively, in comparison with the solubility of $\text{ThO}_2(\text{am, hyd})$ under these conditions. The results of [1973DER/FAU3] are consistent with the solubility and speciation calculated with the equilibrium constants selected in this review. The limiting carbonate complex is the dominant species under the experimental conditions of [1973DER/FAU3], while at higher pH the ternary complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$ becomes the dominant aqueous species and $\text{ThO}_2(\text{am, hyd})$ the solubility limiting solid phase. Figure XI-7 shows that the somewhat higher solubility of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ in 1 M Na_2CO_3 compared to that in 1 M $\text{NaHCO}_3 + 1 \text{ M NaNO}_3$ is not caused by the formation of $\text{Th}(\text{CO}_3)_6^{8-}$ as assumed by Dervin and Faucherre, but by the variation of the medium composition and increasing ionic strength (*cf.* slight increase of the (105) concentration line in Figure XI-7 with increasing pH), and by the contributions from the complex $\text{Th}(\text{OH})(\text{CO}_3)_4^{5-}$, also increasing with pH (*cf.* the concentration line of (114) and speciation diagrams in Figure XI-7 and Figure XI-8).

Figure XI-7: Solubility and speciation of thorium at a total carbonate concentration of $C_{\text{tot}} = 1.0 \text{ M}$. Experimental data for $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ in $1.0 \text{ M NaHCO}_3 + 1.0 \text{ M NaNO}_3$ and in $1.0 \text{ M Na}_2\text{CO}_3$ [1973DER/FAU3], [1961LUZ/KOV2] and for $\text{ThO}_2(\text{am, hyd})$ in $1.0 \text{ M Na}_2\text{CO}_3$ containing $0.01\text{--}1.0 \text{ M NaOH}$ [1995RAI/FEL], [2005ALT/NEC]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review taking into account the variation of the solution composition and ionic strength.

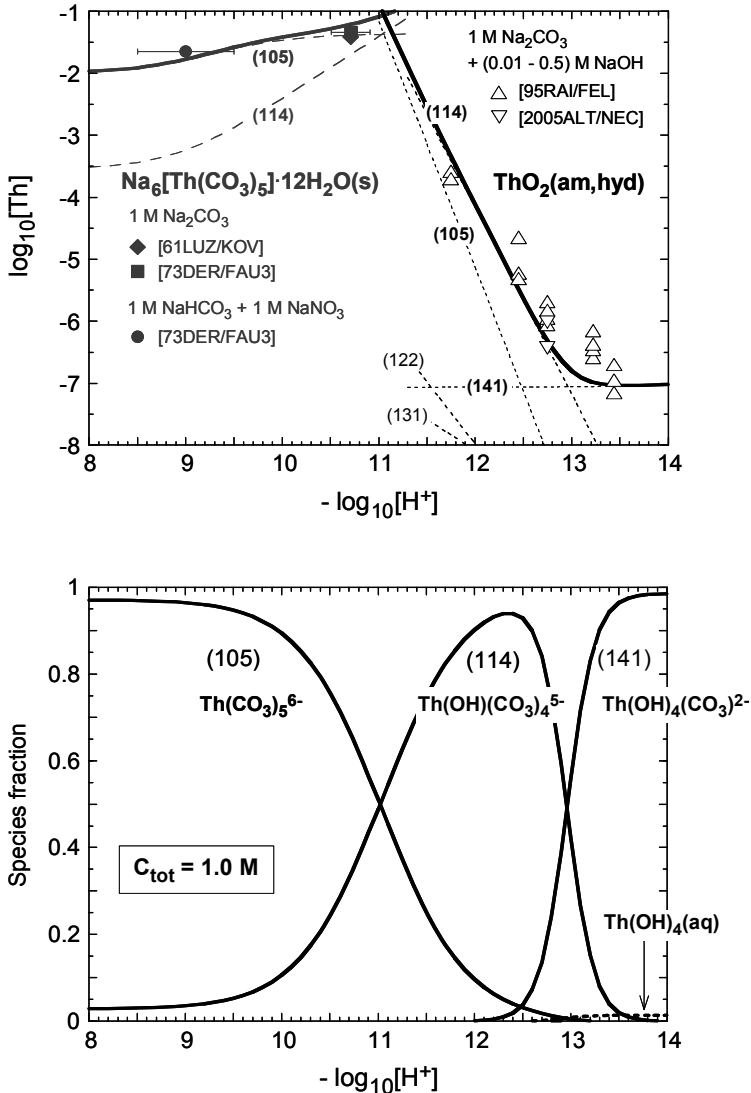
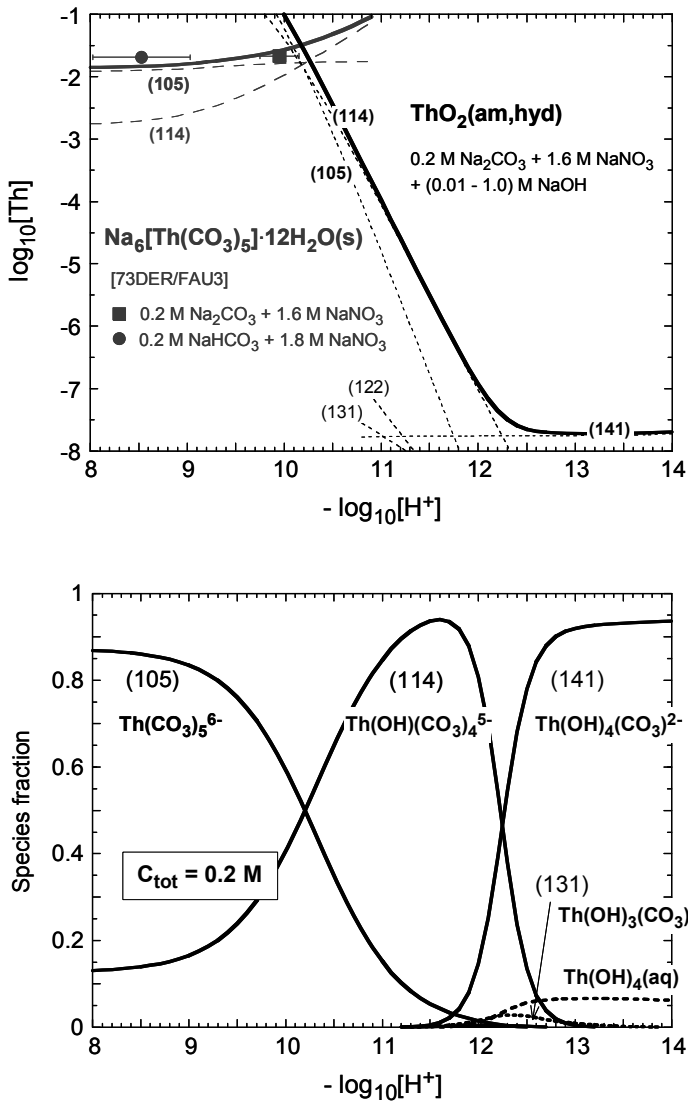
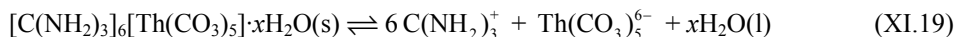


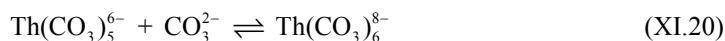
Figure XI-8: Solubility and speciation of thorium at a total carbonate concentration of $C_{\text{tot}} = 0.2 \text{ M}$. Experimental data for $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ in $0.2 \text{ M NaHCO}_3 / 1.8 \text{ M NaNO}_3$ and in $0.2 \text{ M Na}_2\text{CO}_3 / 1.6 \text{ M NaNO}_3$ [1973DER/FAU3] and calculated solubility for $\text{ThO}_2(\text{am,hyd})$ in $0.2 \text{ M Na}_2\text{CO}_3 / 1.6 \text{ M NaNO}_3$ containing $0.01\text{--}1.0 \text{ M NaOH}$. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review taking into accounting the variation of the solution composition and ionic strength.



Dervin and Faucherre [1973DER/FAU3] have also measured the solubility of $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5] \cdot x\text{H}_2\text{O}(\text{s})$ as function of the carbonate and bicarbonate concentration, using a guanidinium nitrate ionic medium. The $\text{C}(\text{NH}_2)_3^+$ concentration was kept constant at 2.0 M. In the 2.0 M $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3\text{-C}(\text{NH}_2)_3\text{NO}_3$ solutions with $[\text{HCO}_3^-]$ in the range 0.2–1.0 M, the solubility of $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5] \cdot x\text{H}_2\text{O}(\text{s})$ remained constant at 1.57×10^{-3} M, yielding a conditional equilibrium constant of: $K_{s,5}(\text{XI.19}) = [\text{C}(\text{NH}_2)_3^+]^6 [\text{Th}(\text{CO}_3)_5^{6-}] = 0.10 \text{ M}^7$ for the reaction:



In the $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3\text{-C}(\text{NH}_2)_3\text{NO}_3$ solutions with $[\text{C}(\text{NH}_2)_3^+] = 2.0 \text{ M}$ and $[\text{CO}_3^{2-}] = 0.25\text{--}1.0 \text{ M}$ the ionic strength varies from $I = 2.25$ to 3.0 M. The solubility remained constant at 1.7×10^{-3} M, in the range $0.25 \text{ M} < [\text{CO}_3^{2-}] < 0.35 \text{ M}$, indicating the predominance of $\text{Th}(\text{CO}_3)_5^{6-}$ in solution and a very similar value of $K_{s,5} = 0.11 \text{ M}^7$. At carbonate concentrations above 0.35, M the solubility increases and the slope of $\log_{10} [\text{Th}]_{\text{tot}}$ vs. $\log_{10} [\text{CO}_3^{2-}]$ apparently indicates an equilibrium between $\text{Th}(\text{CO}_3)_5^{6-}$ and $\text{Th}(\text{CO}_3)_6^{8-}$:



As discussed above for the solubility of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ in the corresponding $\text{Na}_2\text{CO}_3\text{-NaNO}_3$ and $\text{NaHCO}_3\text{-NaNO}_3$ solutions, it is clear that the activity coefficients do not remain constant at these high and varying carbonate concentrations. This review therefore does not accept the interpretation given by Dervin and Faucherre and concludes that the limiting Th(IV) carbonate complex is $\text{Th}(\text{CO}_3)_5^{6-}$, a conclusion that is supported by the available EXAFS data.

The solubility of $[\text{C}(\text{NH}_2)_3]_6[\text{Th}(\text{CO}_3)_5] \cdot x\text{H}_2\text{O}(\text{s})$ is about 10 times lower than that of $\text{Na}_6[\text{Th}(\text{CO}_3)_5] \cdot 12\text{H}_2\text{O}(\text{s})$ in the corresponding sodium salt solutions. It is not possible to extrapolate the conditional solubility constant $\log_{10} K_{s,5} = -1.0$ at $I = 2.0 \text{ M}$ to zero ionic strength, because the ion interaction coefficients between $\text{C}(\text{NH}_2)_3^+$ and NO_3^- , HCO_3^- , CO_3^{2-} , and $\text{Th}(\text{CO}_3)_5^{6-}$ are not known.

XI.1.3.4 Additional studies of the thorium carbonate system

Bruno *et al.* [1987BRU/CAS2] and Grenthe and Lagerman [1991GRE/LAG2] performed potentiometric studies of the Th(IV)-hydroxide-carbonate system under CO_2 partial pressures of 0.3 and 1.0 bar ($[\text{Th}]_{\text{tot}} = 0.24\text{--}7.0 \text{ mM}$, $-\log_{10} [\text{H}^+] = 2.5\text{--}5.0$ in 3.0 M NaClO_4). They noticed that the very steep curves of Z (average number of bonded OH^- per Th) vs. $\log_{10} [\text{H}^+]$ indicate the formation of complexes with high nuclearity, e.g. " $\text{Th}_8(\text{OH})_{24}(\text{CO}_2)_2^{8+}$ " \equiv $\text{Th}_8(\text{OH})_{20}(\text{CO}_3)_2^{8+}$ and " $\text{Th}_{16}(\text{OH})_{52}(\text{CO}_2)_{16}^{12+}$ " \equiv $\text{Th}_{16}(\text{OH})_{20}(\text{CO}_3)_{16}^{12+}$ which could explain the data at the lowest Th concentrations [1991GRE/LAG2]. The steep rise in the Z -curves take place at $-\log_{10} [\text{H}^+]$ around 3.3 where there should be no precipitation of Th(IV) hydrous oxide and no significant formation of mononuclear hydroxide-carbonate complexes *cf.*, Appendix A reviews of [1994OST/BRU] and [2005ALT/NEC]. A possible explanation suggested by this review

is that hydrous oxides precipitate on the CO₂ gas-bubbles present in the study, that is a similar process to that used in flotation of ores. There is no attempt to make a quantitative evaluation of the carbonate data in [1991GRE/LAG2] and accordingly no quantitative information on the stoichiometry and equilibrium constants in the ternary Th(IV)-H₂O-CO₂(g) system at pH < 5.

Faucherre and Dervin [1962FAU/DER], [1962FAU/DER2], [1973DER/FAU2] have studied the complex formation in the thorium-carbonate system using different experimental methods. In [1962FAU/DER] they used cryoscopy and concluded that "it appears that the constitution of the complexes in the solutions studied is of the type [Th(CO₃)₅⁶⁻]" ; however no thermodynamic data are given. In a second study [1962FAU/DER2] used potentiometry in attempt to determine the composition of the species formed. The experimental data were not rigorously analysed and no thermodynamic data were derived. In a third study [1973DER/FAU2] used cryoscopy, conductometry and ion exchange, but the information provided is limited to a suggestion that the limiting carbonate complex has the composition [Th(CO₃)₆]⁸⁻, a conclusion not consistent with other observations as discussed in this review. Chernyaev *et al.* [1961CHE/GOL] describe the preparation of (NH₄)₆[Th(CO₃)₅]·3H₂O and its thermal stability, but with no quantitative thermodynamic data. Ryabchikov *et al.* [1963RYA/VOL] have used high frequency titrations to establish that the stoichiometry of the limiting complex is [Th(CO₃)₄]⁴⁻, not consistent with other observations. They also provide some crystallographic and thermogravimetric information. There are no thermodynamic data in this communication. Voliotis *et al.* [1975VOL/RIM2], [1975VOL/RIM3] demonstrate the coordination geometry of [Th(CO₃)₅]⁶⁻ that occurs as isolated complexes in different solid phase of the type M₆[Th(CO₃)₅]·xH₂O; where M is a univalent ion. The carbonate ligand is bonded through two oxygen atoms, resulting in a coordination number of ten for Th⁴⁺. The same stoichiometry has been established in a number of solution chemical experiments at high carbonate concentrations and also in EXAFS studies of the Th(IV) limiting carbonate complex [1997FEL/RAI], [2006ALT/NEC] and the corresponding complexes of U(IV) [1998RAI/FEL], Np(IV) [1999RAI/HES], and Pu(IV) [1998CLA/CON], [1999RAI/HES2].

The mode of coordination of the carbonate ligand in solid phases has been inferred from IR spectra, [1962KAR/VOL], [1969KHA/MOL2] and [1982JOL/THO]; the conclusions in the first two of these studies are not in agreement with the known structure of the phases investigated. The third study made after the structure was known claims that the reported IR data are consistent with bidentate coordination of the carbonate ligand. Tolmachev [1944TOL] used UV spectrophotometry to suggest the formation of Th(OH)₂(CO₃)₄⁶⁻. Only an abstract of this paper was available to the reviewers and the conclusions of this study have therefore not been accepted.

XI.1.3.5 Summary of selected thermodynamic data

The equilibrium constants selected in this review for solid and aqueous thorium carbonate compounds and the corresponding molar standard Gibbs energies of formation are summarised in Table XI-6.

Table XI-6: Equilibrium constants at zero ionic strength and molar standard Gibbs energies of formation selected for solid and aqueous thorium carbonate compounds at 25°C.

Solid phase	$\log_{10} K_{s,0}^{\circ}$	$\log_{10} K_{s,s}^{\circ}$	$\Delta_f G_m^{\circ}$ (kJ·mol ⁻¹)
Na ₆ [Th(CO ₃) ₅]·12H ₂ O(cr)	-42.2 ± 0.8 ^a	-11.2 ± 0.4 ^b	-8002.6 ± 7.3
ThO ₂ (am, hyd, aged)	-47.5 ± 0.9 ^c		
Aqueous complex	$\varepsilon((1yz), \text{Na}^+) \text{ (kg·mol}^{-1}\text{)}$	$\log_{10} \beta_{1z}^{\circ}$ ^d	$\Delta_f G_m^{\circ}$ (kJ·mol ⁻¹)
Th(CO ₃) ₅ ⁶⁻	-0.30 ± 0.15	31.0 ± 0.7	-3521.2 ± 6.9
Th(OH)(CO ₃) ₄ ⁵⁻	-0.22 ± 0.13	35.6 ± 0.5	-3176.8 ± 6.2
Th(OH) ₂ (CO ₃) ₂ ²⁻	-0.1 ± 0.2	36.8 ± 0.5	-2285.1 ± 6.1
Th(OH) ₄ (CO ₃) ₂ ²⁻	-0.1 ± 0.2	40.4 ± 0.6	-2092.2 ± 6.3

a: Reaction: Na₆[Th(CO₃)₅]·12H₂O(s) ⇌ 6Na⁺ + Th⁴⁺ + 5CO₃²⁻ + 12H₂O(l)

b: Reaction: Na₆[Th(CO₃)₅]·12H₂O(s) ⇌ 6Na⁺ + Th(CO₃)₅⁶⁻ + 12H₂O(l)

c: Reaction: ThO₂(am, hyd, aged) + 2H₂O(l) ⇌ Th⁴⁺ + 4OH⁻

d: Reaction: Th⁴⁺ + yOH⁻ + zCO₃²⁻ ⇌ Th(OH)_y(CO₃)_z^{4-y-2z}

XI.1.3.6 Thorium thiocyanate

XI.1.3.6.1 Complexes with SCN⁻

Thiocyanate solutions are extensively used analytically in various metal-metal separation methods, some of which include thorium. However, the quantitative information on chemical equilibria in the aqueous Th(IV)-SCN⁻ system is limited. Experimental investigations have been reported by Waggener and Stoughton [1950WAG/STO], Laubscher and Fouché [1971LAU/FOU], Sato *et al.* [1973SAT/KOT], Manouvrier and Devaure [1978MAN/DEV] and Livet and Musikas [1985LIV/MUS]; the latter study is only available as a conference contribution, *cf.* Appendix A.

The results reported by Waggener and Stoughton [1950WAG/STO] were given only in an ORNL quarterly report without any details and therefore could not be evaluated by this review. However, their value of $\beta_1 = 12.1 \text{ M}^{-1}$ ($\log_{10} \beta_1 = (1.08 \pm 0.08)$) listed in Table XI-7, recalculated to $I = 0$, $\log_{10} \beta_1^{\circ} = (2.44 \pm 0.16)$, is in fair agreement with the value $\log_{10} \beta_1^{\circ} = (2.0 \pm 0.5)$ from [1971LAU/FOU] selected by this review.

The equilibrium analysis in [1971LAU/FOU] was based on measurements of the distribution of trace amounts of Th(IV) between an aqueous phase containing different concentrations of thiocyanate and a benzene phase containing the extracting

ligand, thenoyltrifluoroacetone (TTA) or dinonyl naphthalene sulphonic acid (DNNS). The hydrogen ion concentration was sufficiently high to prevent significant amounts of hydroxide complexes to be formed. The experimental distribution data cover the concentration range $0.00 \text{ M} < [\text{SCN}^-] < 1.00 \text{ M}$ in the TTA system and $0.00 \text{ M} < [\text{SCN}^-] < 2.50 \text{ M}$ in the DNNS system, respectively. The equilibrium constants deduced from these data are given in Table XI-7.

Table XI-7: Equilibrium constants deduced from the studies of [1971LAU/FOU], [1950WAG/STO] and [1985LIV/MUS].

Method	Ionic strength ($\text{mol}\cdot\text{L}^{-1}$)	β_1 ($\text{mol}\cdot\text{L}^{-1}$) ⁻¹	β_2 ($\text{mol}\cdot\text{L}^{-1}$) ⁻²	β_3 ($\text{mol}\cdot\text{L}^{-1}$) ⁻³	β_4 ($\text{mol}\cdot\text{L}^{-1}$) ⁻⁴	References
DNNS	3.0 ^a	7.12 ± 1.11	33.9 ± 5.3	14.3 ± 7.3	32.4 ± 2.7	[1971LAU/FOU]
TTA	3.0 ^a	9.01 ± 0.62	25.1 ± 2.7	5.8 ± 2.6	-	[1971LAU/FOU]
TTA	1.0 ^a	12.1	60	-	-	[1950WAG/STO]
Raman spectroscopy	varying	25 ± 9	-	186 ± 39	-	[1978MAN/DEV]
Raman spectroscopy	varying, pH not reported	4.0 ± 0.6	5.0 ± 0.1	5.4 ± 0.1	1.4 ± 0.1	[1985LIV/MUS]

a: $[\text{H}^+] = 0.50 \text{ M}$ in $(\text{H}^+/\text{Na}^+)(\text{SCN}^-/\text{ClO}_4^-)$ media.

The values of β_1 and β_2 are in fair agreement between the two extraction systems, while the discrepancy is larger for β_3 and β_4 ; the authors suggest that this might be due to the formation of mixed Th(IV)-SCN⁻-TTA complexes in the aqueous phase, but this is an *ad hoc* assumption. A large part of the ClO₄⁻ in the ionic medium has been replaced by SCN⁻ in the range where β_3 and β_4 are determined, the equilibrium constants might then be strongly influenced by activity factor variations resulting from the changes in the ionic medium. The data in [1985LIV/MUS] have been made in a medium with variable ionic strength, in addition there is no information of the pH in the test solutions; the data have therefore not been accepted by this review.

This review has only accepted the values of β_1 and β_2 from [1971LAU/FOU] and selected their average and an uncertainty range that covers their respective uncertainties, $\beta_1 = (8.0 \pm 1.5) (\text{mol}\cdot\text{L}^{-1})^{-1}$, $\beta_2 = (30 \pm 10) (\text{mol}\cdot\text{L}^{-1})^{-2}$, $\log_{10} \beta_1 = (0.90 \pm 0.08)$ and $\log_{10} \beta_2 = (1.48 \pm 0.14)$ at $I = 3.0 \text{ M}$. However the study by Sato *et al.*[1973SAT/KOT] strongly suggests that complexes with four or more coordinated ligands are formed at high SCN⁻ concentrations. Manouvrier and Devaure [1978MAN/DEV] have studied the complex formation in the Th(IV) thiocyanate system using Raman spectroscopy. The experiments have been made at different pressures ranging from 0.1 – 300 MPa, by varying the ratio between SCN⁻ and Th(IV) using high total concentrations of the reactants. The experimental data show conclusively that the SCN⁻ ligand is coordinated through the nitrogen donor, but the deduction of the

stoichiometry and equilibrium constants of the complexes formed is less clear; Manouvrier and Devaure report the formation of $\text{Th}(\text{SCN})_3^{3+}$ and $\text{Th}(\text{SCN})_3^+$ with equilibrium constants $\beta_1 = (25 \pm 9) (\text{mol}\cdot\text{L}^{-1})^{-1}$ and $\beta_3 = (186 \pm 39) (\text{mol}\cdot\text{L}^{-1})^{-3}$, respectively at 0.1 MPa. There is no indication in the studies of [1950WAG/STO] and [1971LAU/FOU] that $\text{Th}(\text{SCN})_2^{2+}$ is a weak complex and this review suggests that its absence in the chemical model used in [1978MAN/DEV] is an artefact. The equilibrium constant for the first complex is consistent with values in [1950WAG/STO] and [1971LAU/FOU].

This review has based the selected equilibrium constants for the formation of $\text{Th}(\text{SCN})_3^{3+}$ and $\text{Th}(\text{SCN})_2^{2+}$ solely on the data from [1971LAU/FOU] in a 3.0 M perchlorate ionic medium. They have been recalculated to zero ionic strength using the ion interaction parameters $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon(\text{Na}^+, \text{SCN}^-) = (0.05 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ and assuming $\varepsilon(\text{Th}(\text{SCN})_3^{3+}, \text{ClO}_4^-) = (0.50 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon(\text{Th}(\text{SCN})_2^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Np}(\text{SCN})_2^{2+}, \text{ClO}_4^-) = (0.38 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$.

The equilibrium constants and standard molar Gibbs energy of reaction for the formation of $\text{Th}(\text{SCN})_3^{3+}$ and $\text{Th}(\text{SCN})_2^{2+}$ selected by this review are:

$$\log_{10} \beta_1^\circ = (2.0 \pm 0.5); \Delta_r G_m^\circ = -(11.4 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10} \beta_2^\circ = (3.4 \pm 0.8); \Delta_r G_m^\circ = -(19.4 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainty is primarily due to the uncertainties of the SIT coefficients used for the extrapolation to $I = 0$.

The Gibbs energies of formation of $\text{Th}(\text{SCN})_3^{3+}$ and $\text{Th}(\text{SCN})_2^{2+}$ have been calculated from the selected values of the Gibbs energy of reaction and the selected Gibbs energy of formation of Th^{4+} and SCN^- :

$$\Delta_f G_m^\circ(\text{Th}(\text{SCN})_3^{3+}, 298.15 \text{ K}) = -(623.5 \pm 7.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th}(\text{SCN})_2^{2+}, 298.15 \text{ K}) = -(538.8 \pm 10.6) \text{ kJ}\cdot\text{mol}^{-1}.$$

There is no information on the enthalpy and entropy of reaction for the species formed in the Th(IV)-thiocyanate system.

XI.2 Silicon compounds and complexes

XI.2.1 Solid thorium silicides

There are four well-established intermetallic phases in this system, Th_3Si_2 , ThSi , Th_3Si_5 and ThSi_2 . The structural data on these compounds have been assembled by [1981CHI/AKH] and are shown in Table XI-8. In addition Brown and Norreys [1960BRO/NOR] found evidence for a phase of composition $\text{Th}_6\text{Si}_{11}$, with two polymorphs with a transition temperature of *ca.* 1573 K. The structural data in Table XI-8 suggest that they are defect structures of ThSi_2 .

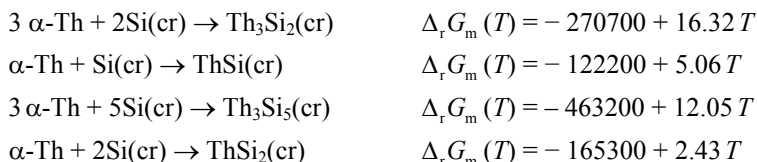
Table XI-8: Structural data for thorium silicides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)
Th ₃ Si ₂	Tetragonal <i>P4/mbm</i>	U ₃ Si ₂	$a = 7.289$ $c = 4.149$
ThSi	orthorhombic <i>Pnma</i>	FeB	$a = 7.88$ $b = 4.148$ $c = 5.896$
Th ₃ Si ₅	hexagonal <i>P6/mmm</i>	AlB ₂	$a = 3.897 - 3.896$ $c = 4.204 - 4.228$
Th ₆ Si ₁₁ < <i>ca.</i> 1573 K	hexagonal <i>P6/mmm</i>	AlB ₂	$a = 4.013$ $c = 4.258$
Th ₆ Si ₁₁ > <i>ca.</i> 1573 K	tetragonal <i>I4₁/amd</i>	ThSi ₂	$a = 4.01$ $c = 13.89$
ThSi ₂ < <i>ca.</i> 1573 K	hexagonal <i>P6/mmm</i>	AlB ₂	$a = 4.136$ $c = 4.126$
ThSi ₂ > <i>ca.</i> 1573 K	tetragonal <i>I4₁/amd</i>	ThSi ₂	$a = 4.135$ $c = 14.375$

There are two measurements of the enthalpy of formation of ThSi₂(cr) by direct combination of the elements in a calorimeter, by Robins and Jenkins [1955ROB/JEN] at 296 K and by Wang *et al.* [2000WAN/GUO] at 298.15 K. Fuller details are given in Appendix A. Neglecting the small difference in temperature, the average of three individual measurements by [1955ROB/JEN], using 98.7% pure thorium samples, yielded: $\Delta_f H_m^\circ(\text{ThSi}_2, \text{cr}, 298.15\text{K}) = -(174.3 \pm 15.9) \text{ kJ}\cdot\text{mol}^{-1}$, where the uncertainty is calculated by this review. Wang *et al.* [2000WAN/GUO], made six measurements using purer (99.8%) thorium to give an average of $\Delta_f H_m^\circ(\text{ThSi}_2, \text{cr}, 298.15\text{K}) = -(166.8 \pm 12.0) \text{ kJ}\cdot\text{mol}^{-1}$. The uncertainty limits reported by the authors have been doubled here so as to represent the 95% confidence interval.

The other thermodynamic data for thorium silicides are the Knudsen effusion measurements of silicon pressures from *ca.* 1685–1961 K in various diphasic fields by [1966ALC/COR]. As discussed in Appendix A, the only practical route to utilising these data is to adopt the activities, and thus Gibbs energy data, given by these authors, rather than try to reassess them, since this removes some the experimental uncertainty in the decomposition pressures. Even then there is some ambiguity in the results, since [1966ALC/COR] only define the Gibbs energies from Th(cr) and Si(cr), without defining the thorium allotrope, although the measurements span the α – β transformation temperature. The data given by [1981CHI/AKH], specified to be for the formation from α -Th and Si(l) seem to be derived from the values in [1966ALC/COR] assuming the latter refer to formation from α -Th, and we have made the same assumption, without further processing.

Given the ambiguity in the data, the following values, valid for 1685 to 1961 K, are given for information only.



The value of the enthalpy of formation of $\text{ThSi}_2(\text{cr})$, $-165.3 \text{ kJ}\cdot\text{mol}^{-1}$ from these high temperature measurements (*ca.* 1750 K) supports the consistent calorimetric values determined near room temperature, noted above. The selected value is the weighted mean of the two calorimetric values:

$$\Delta_f H_m^\circ(\text{ThSi}_2, \text{cr}, 298.15 \text{ K}) = -(169.5 \pm 9.6) \text{ kJ}\cdot\text{mol}^{-1}.$$

XI.2.2 Thorium silicate, $\text{ThSiO}_4(\text{cr})$

$\text{ThSiO}_4(\text{cr})$ exists in two polymeric forms, thorite and huttonite. Thorite is tetragonal with $a = 7.1328 \text{ \AA}$, $c = 6.3188 \text{ \AA}$, [1978TAY/EWI], while huttonite is monoclinic, with $a = 6.80 \text{ \AA}$, $b = 6.96 \text{ \AA}$, $c = 6.54 \text{ \AA}$, $\beta = 104.55^\circ$, [1951PAB/HUT]. However, the precise form of the polymorphism is still not clear. Huttonite is certainly the stable form at high temperatures and pressures, and there are two independent studies, [1964FIN/HAR] and [1997SEY/MON] which suggest that the equilibrium temperature is *ca.* $(1490 \pm 10) \text{ K}$, while in another study [1964DAC/ROY] the transformation is located at about 1273 K. The higher temperature range is supported by the recent results of Mazeina *et al.* [2005MAZ/USH] (see below and Appendix A) on the synthesis temperatures for the two forms.

There seems to be no direct evidence, however, that huttonite has ever been converted, even partially, to thorite under any conditions and indeed, Mumpton and Roy [1961MUM/ROY] have suggested that thorite may possibly be metastable at all temperatures and pressures despite its ready formation at temperatures below *ca.* $(1490 \pm 10) \text{ K}$.

Mazeina *et al.* [2005MAZ/USH] have obtained the standard enthalpies of formation of the two forms of thorite and huttonite, and, independently, the enthalpy of transition between these two polymorphs from high temperature calorimetry. Results were reported as averages of several experiments.

Crystals of the compounds were grown by the thermal gradient flux technique using $\text{Li}_2\text{O}\cdot 2\text{WO}_3$ as solvent, at 1473 K for thorite and at 1673 K for huttonite, from $\text{SiO}_2(\text{cr}, \alpha\text{-quartz})$ with a reported purity greater than 99.9% and $\text{ThO}_2(\text{cr})$ with a reported purity greater than 99.99% (on the basis of the thorium content), thoroughly dried before use. Microprobe analyses indicated that the compounds were nearly stoichiometric – see Appendix A for details. Measurements of the enthalpy difference of samples of thorite and huttonite between 298.15 and 1774 K gives the enthalpy of the

transition of thorite to huttonite, since thorite is transformed into huttonite at the high temperature. The experimental data give a value of $\Delta_{\text{trs}}H_m$ ((XI.21), 298.15 K) = (7.2 ± 7.4) kJ·mol⁻¹ (see Appendix A) for the reaction:



with the assumption that the heat capacities of the two polymorphs are the same.

For the determination of the enthalpies of formation of the two isomorphs, a custom-built Tian-Calvet calorimeter was used, operating at 1080 K. The solvent, contained in a platinum crucible, was 2PbO·B₂O₃. The reported results are derived from experiments in which samples at room temperature (25°C) were dropped into the solvent at the calorimeter temperature.

For the reactions



and



values of $\Delta_f H_m^\circ$ ((XI.22), 298.15 K) = (19.6 ± 2.0) kJ·mol⁻¹ and $\Delta_f H_m^\circ$ ((XI.23), 298.15 K) = (26.3 ± 3.0) kJ·mol⁻¹ were obtained, giving for the transition:



$\Delta_{\text{trs}}H_m^\circ$ ((XI.21), 298.15 K) = (6.7 ± 3.6) kJ·mol⁻¹, a value in agreement with that obtained from the heat content measurements, but more precise and involving fewer assumptions.

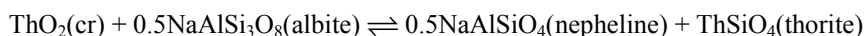
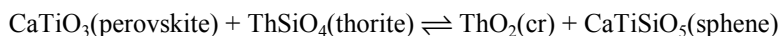
According to these results, both compounds are metastable towards quartz and thorium dioxide under standard conditions.

Use of the values selected in this review for $\Delta_f H_m^\circ$ (ThO₂, cr, 298.15K) = $-(1226.4 \pm 3.5)$ kJ·mol⁻¹ and $\Delta_f H_m^\circ$ (SiO₂, α -quartz, 298.15 K) = $-(910.7 \pm 1.0)$ kJ·mol⁻¹ yields the values:

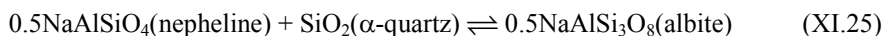
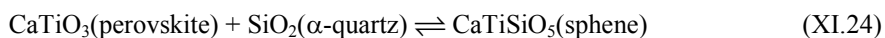
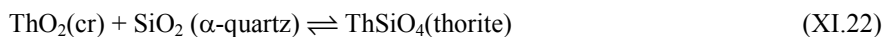
$$\Delta_f H_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2117.5 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThSiO}_4, \text{huttonite}, 298.15 \text{ K}) = -(2110.8 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$$

Schuling *et al.* [1976SCH/VER] have estimated the Gibbs energy of formation of thorite at 1000K and 1 kbar pressure. In a series of compatibility experiments, they found that the two reactions:



both have $\Delta_f G_m < 0$ at 1000 K and 1 kbar. From this, they infer that for the following reactions:



$\Delta_r G_m$ (XI.24) < $\Delta_r G_m$ (XI.22) < $\Delta_r G_m$ (XI.25) at 1000 K and 1 kbar.

We have used data from Robie and Hemingway [1995ROB/HEM] for reactions (XI.24) and (XI.25) to give the values in Table XI-9.

Table XI-9: Limiting Gibbs energies of reaction

Reaction	$\Delta_r G_m$ (1000 K, 1 bar) (kJ·mol ⁻¹)	$\Delta_r G_m$ (1000 K, 1 kbar) (kJ·mol ⁻¹)
(XI.24)	-15.90 ± 3.70	-15.96 ± 3.70
(XI.25)	-9.70 ± 2.60	-9.67 ± 2.60
(XI.22)	-12.77 ± 6.84	-12.82 ± 6.84*

*: Mean of $\Delta_r G_m$ (XI.24) and $\Delta_r G_m$ (XI.25).

This study would thus suggest that the value of $\Delta_r G_m$ ((XI.22), 1000 K, 1 bar) is $-(12.8 \pm 6.8)$ kJ·mol⁻¹. Since there are no values for the heat capacity of thorite, this value cannot be extrapolated to 298.15 K. However, comparison with the enthalpy of this reaction reported by [2005MAZ/USH], noted above, $\Delta_r H_m$ ((XI.22), 298.15 K) = 19.6 kJ·mol⁻¹, indicates that the entropy of Reaction (XI.22) is distinctly positive.

The only selected values are the enthalpies of formation from the study by [2005MAZ/USH]:

$$\Delta_f H_m^\circ(\text{ThSiO}_4, \text{thorite}, 298.15 \text{ K}) = -(2117.5 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThSiO}_4, \text{huttonite}, 298.15 \text{ K}) = -(2110.8 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$$

XI.2.3 Aqueous complexes with H₄SiO₄(aq) and polynuclear Si species

No thermodynamic data for this system are available. However, X-ray absorption studies [2005RAI/YUI] of aqueous solutions in the Th-Si system under acidic conditions (pH ~ 1) and the solubility of ThO₂·xH₂O in highly alkaline conditions (pH 11–12) in the presence of ≥ 0.08 M soluble Si concentrations [2002PER/RIG] strongly suggest that thorium forms fairly strong complexes with silicate ions under these conditions. As discussed in Appendix A, the analysis of [2002PER/RIG] is far from unambiguous. However, one cannot exclude the formation of thorium complexes with polymeric silicate species and additional studies are necessary in order to decide if complexes of this type might be important at the high pH encountered in cement lined repositories.

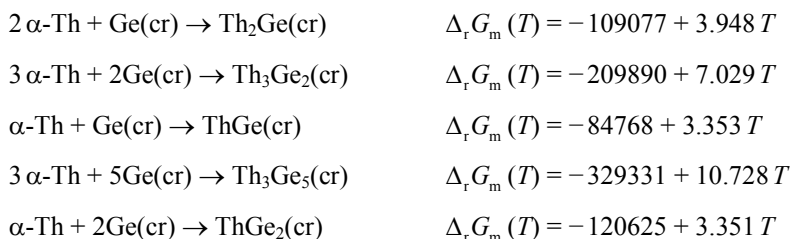
XI.3 Thorium germanides

The phase diagram, structures and thermodynamic data have been treated by [1981CHI/AKH], and since there has been no further work published on this system, the present treatment follows closely their review. The phase diagram is still not well established, particularly around the ThGe₂ composition. The phases in Table XI-10 have been identified with some certainty, except that the high temperature polymorphism of ThGe₂ is not firmly established. The structural data are those quoted by [1981CHI/AKH], with some minor corrections from [1975FER].

Table XI-10: Structural data for thorium germanides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)
Th ₂ Ge	tetragonal, <i>I4/mcm</i>	Al ₂ Cu	<i>a</i> = 7.414 <i>c</i> = 6.081
Th ₃ Ge ₂	tetragonal, <i>P4/mbm</i>	U ₃ Si ₂	<i>a</i> = 7.95 – 7.98 <i>c</i> = 4.19 – 4.17
ThGe	fcc, <i>Fm$\bar{3}m$</i>	NaCl	<i>a</i> = 6.05 – 6.041
Th ₃ Ge ₅	hexagonal <i>P6/mmm</i>	AlB ₂	<i>a</i> = 4.065 <i>c</i> = 4.202
ThGe ₂ < <i>ca.</i> 877 K	orthorhombic, <i>Cmcm</i>	AlB ₂	<i>a</i> = 4.223 <i>b</i> = 16.911 <i>c</i> = 4.052
ThGe ₂ high temperature phase	tetragonal <i>I4/amd</i>	ThSi ₂	<i>a</i> = 4.13 – 4.18 <i>c</i> = 14.20 – 14.23
Th _{0.9} Ge ₂	orthorhombic, <i>Cm$\bar{3}m$</i>	ZrSi ₂	<i>a</i> = 4.160 <i>c</i> = 16.642 <i>c</i> = 4.023

There are two sets of thermodynamic data for thorium germanides, which are not in good agreement. Wang *et al.* [2000WAN/GUO] measured the enthalpy of formation of ThGe₂(cr) at 298.15 K by direct combination of the elements (at 1473 K), as described in Appendix A. The average of six measurements gave $\Delta_f H_m^\circ(\text{ThGe}_2, \text{cr}, 298.15 \text{ K}) = -(216.6 \pm 8.4) \text{ kJ}\cdot\text{mol}^{-1}$, where the authors' uncertainty limits have been doubled to correspond to a 95% uncertainty. The other data are the Knudsen effusion measurements of germanium pressures from *ca.* 1330–1500 K in various diphasic fields by [1966ALC/COR]. However, as noted by [1981CHI/AKH], [1966ALC/COR] took the composition of the most Th-rich phase to be Th₃Ge, rather than the now established composition of Th₂Ge, and the most Ge-rich phase to be ThGe₂ rather than Th_{0.9}Ge₂. Chiotti *et al.* [1981CHI/AKH] have reinterpreted the measurements of [1966ALC/COR] to accord with the currently accepted phase diagram. Their revised values for the Gibbs energy of formation of the phases from 1330–1500 K are



It will be seen that the enthalpy of formation of $\text{ThGe}_2(\text{cr})$ around 1400 K, $-120.6 \text{ kJ}\cdot\text{mol}^{-1}$, derived from these measurements is very much less negative than the directly determined value noted above. It is difficult to explain this large discrepancy, especially as the data for $\text{ThSi}_2(\text{cr})$ from the two same studies agree rather well, as noted in Section XI.2.1. No values have been selected by the review for the thorium germanide phases.

XI.4 Thorium-tin compounds

Cirafici *et al.* [1983CIR/PAL] have studied the Th-Sn system, and no new phases have been reported since then.

There are four phases in the system, with structures given in Table XI-11 [1983CIR/PAL].

Table XI-11: Structural data for thorium tin compounds.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)
Th_5Sn_3	hexagonal, $P6_3/mcm$	Mn_5Si_3	$a = 9.332$ $c = 6.477$
Th_5Sn_4	hexagonal, $P6_3/mcm$	Ti_5Ga_4	$a = 9.643$ $c = 6.445$
ThSn_2	orthorhombic $Cmcm$	ZrSi_2	$a = 4.463$ $b = 17.062$ $c = 4.379$
ThSn_3	cubic, $Pm\bar{3}m$	AuCu_3	$a = 4.719$

For $\text{ThSn}_3(\text{cr})$, the results of [1983CIR/PAL] confirmed the structural data obtained earlier by [1958FER] who had reported $a = 4.718 \text{ \AA}$, while [1970HAV/DAM] gave $a = 4.714 \text{ \AA}$. This compound is isomorphous with USn_3 , ThPb_3 , ThTl_3 , and ThIn_3 . The most stable phase is Th_5Sn_3 , which melts congruently at *ca.* 2073 K.

There are three thermodynamic measurements in this system, two involving $\text{ThSn}_3(\text{cr})$ and one $\text{Th}_5\text{Sn}_3(\text{cr})$. Kadochnikov *et al.* [1977KAD/LEB] measured the emf of the cell:

Th(cr) | KCl-NaCl-3 wt%ThCl₄ | KCl-NaCl-3 wt%ThCl₄ | Sn-Th(l) + compound

from 952 to 1130 K. The actual compound present in the saturated solution was not identified, but was presumably ThSn₃(cr), since Cirafici *et al.* [1983CIR/PAL] report that this is stable up to 1228 K, where it undergoes a peritectic reaction to ThSn₂(cr) and liquid. The thorium potential in the diphasic region {Sn-Th(l) + ThSn₃(cr)} was given by:

$$[\Delta_f G_m]_{950K}^{1130K}(T) = -206517 + 51.677 T \quad \text{J}\cdot\text{mol}^{-1}$$

These data cannot be processed further without an assumption regarding the activity of tin in the saturated Sn-Th liquid. With the low solubility of thorium in Sn(l), also measured by [1977KAD/LEB] to be $\log_{10} x_{\text{Th}} = -4330/T + 2.2360$ from 950 to 1130 K, the chemical potential of tin in the melt will be close to the ideal value and if ThSn₃(cr) is indeed the phase in equilibrium with the saturated liquid, its Gibbs energy of formation (from Sn(l)) in the temperature range of the study by [1977KAD/LEB] is then calculated to be

$$[\Delta_f G_m]_{950K}^{1130K}(\text{ThSn}_3, \text{cr}, T) = -203377 + 48.762 T \quad \text{J}\cdot\text{mol}^{-1}$$

Kadochnikov *et al.* [1977KAD/LEB] estimated the uncertainties in the thorium potential to be only $\pm 400 \text{ J}\cdot\text{mol}^{-1}$, but the uncertainty in the enthalpy values is much higher, $\pm 6300 \text{ J}\cdot\text{mol}^{-1}$, as quoted by authors.

Palenzola and Cirafici [1975PAL/CIR] have measured the enthalpies of formation of ThSn₃(cr) by dynamic differential calorimetry (integration of DTA curves) from an appropriate mixture of the elements, held in a molybdenum container. As discussed in Appendix A, the DTA peak reached its maximum at 793 K. Palenzola and Cirafici [1975PAL/CIR] report the value of $\Delta_f H_m^\circ(\text{ThSn}_3, \text{cr}) = -(162 \pm 16) \text{ kJ}\cdot\text{mol}^{-1}$ to be that at 298.15 K, but make no mention of any corrections applied to the experimental value. We have therefore assumed the value to be that at the maximum in the DTA peak, 793 K and have doubled the uncertainty stated by the authors. However, in view of the uncertainties in the processing of the data from both these studies, these values are quoted for information only.

More recently Wang *et al.* [2000WAN/GUO] have measured the enthalpy of formation of the most stable compound in the system, Th₅Sn₃(cr). They used a direct reaction calorimeter operating at $(1473 \pm 2) \text{ K}$. All samples were held in BN crucibles in an argon atmosphere. For each run, both the unreacted mixture and the actual final product were dropped from 298.15 K to the reacting temperature and the enthalpies measured; the difference between these values therefore gives the enthalpy of formation at 298.15 K. For Th₅Sn₃(cr), the resultant value from six runs was:

$$\Delta_f H_m^\circ(\text{Th}_5\text{Sn}_3, \text{cr}, 298.15 \text{ K}) = -(510.4 \pm 32.0) \text{ kJ}\cdot\text{mol}^{-1}$$

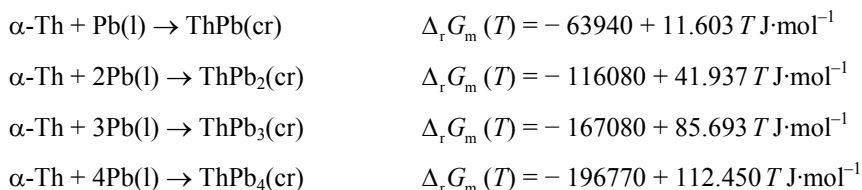
where the authors' uncertainty limits have been doubled to correspond to a 95% uncertainty, and this is the selected value.

As expected from the phase diagram, the enthalpy of formation per gram-atom, $-(63.8 \pm 2.0) \text{ kJ} \cdot (\text{gram-atom})^{-1}$ is appreciably more negative than that for $\text{ThSn}_3(\text{cr})$, *ca.* $-40 \text{ kJ} \cdot (\text{gram-atom})^{-1}$ from the studies noted above.

XI.5 Thorium-lead compounds

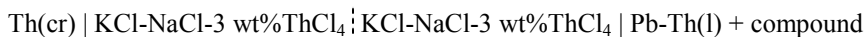
There are three well-established compounds in this system, ThPb , ThPb_2 and ThPb_3 ; in addition, Gans *et al.* [1966GAN/KNA] found evidence for a phase of composition close to ThPb_4 . The structures of ThPb_2 and ThPb_4 are not known; ThPb is body-centred tetragonal, space group $I4_1/amd$, with $a = (4.545 \pm 0.001) \text{ \AA}$, $c = (11.288 \pm 0.006) \text{ \AA}$, [1961BRO] while ThPb_3 is cubic, space group $Pm\bar{3}m$, AuCu_3 type. Values of $a = (4.855 \pm 0.001) \text{ \AA}$ [1958FER], [1961BRO] and 4.853 \AA [1970HAV/DAM] have been reported.

The main thermodynamic data for this system are derived from the Knudsen effusion study by Gans *et al.* [1966GAN/KNA], who measured the vapour pressure of pure lead from 908 to 1178 K and the lead decomposition pressures in the four diphasic fields involving Th, ThPb , ThPb_2 , ThPb_3 and ThPb_4 , from 910 to 1263 K, depending on the phase field. Their measured vapour pressure of lead is in good agreement with the values derived from [1989COX/WAG]. Chiotti *et al.* [1981CHI/AKH] have reassessed these data, making small corrections to the derived equations for the decomposition pressures to obtain better agreement with the phase diagram. We have confirmed that the assessed values of [1981CHI/AKH] give a more consistent description of the system, and have adopted their derived values for the Gibbs energies of formation (from Pb(l)) of the four solid compounds, valid from *ca.* 900 to 1300 K:

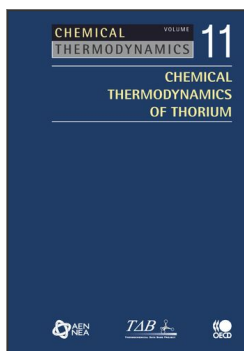


Palenzona and Cirafici [1975PAL/CIR] have measured the enthalpy of formation of $\text{ThPb}_3(\text{cr})$ by dynamic differential calorimetry from a mixture of the elements under experimental conditions identical to those reported for $\text{ThSn}_3(\text{cr})$ (Section XI.4) and discussed in Appendix A. They report the value of $\Delta_f H_m^\circ(\text{ThPb}_3, \text{cr}) = -(117 \pm 12) \text{ kJ} \cdot \text{mol}^{-1}$ to be that at 298.15 K, but make no mention of any correction applied to the experimental value. For this reason, we have doubled the uncertainty stated by the authors. Nevertheless, in view of these uncertainties in processing the data, the results of [1975PAL/CIR] are quoted for information only.

Poyarkov *et al.* [1976POY/LEB] have measured the solubility of thorium in Pb(l) , and the thorium activities in saturated solutions, from 949 to 1043 K using the concentration cell of the type:



The actual compound present in the saturated solution was not identified, but is assumed by this review to be $\text{ThPb}_4(\text{cr})$, as indicated by Gans *et al.* [1966GAN/KNA]. The solubility of thorium in lead in this temperature range is very small (0.23 at% at 1000 K), so the Gibbs energy of formation of $\text{ThPb}_4(\text{cr})$ (from Pb(l)) will be negligibly different from the thorium activity derived from the emf measurements, and thus $\Delta_f G_m(\text{ThPb}_4, \text{cr}, T) = -151870 + 56.646 T \text{ J}\cdot\text{mol}^{-1}$, in the temperature range 949–1043 K. This gives a Gibbs energy of formation of $-95.24 \text{ kJ}\cdot\text{mol}^{-1}$ at 1000 K, compared to $-84.32 \text{ kJ}\cdot\text{mol}^{-1}$ from the pressure measurements of Gans *et al.*; the derived enthalpies and entropies of formation are also notably different. The latter data from the more complete study are preferred, but none of these values can be selected until the discrepancy is resolved.



From:
Chemical Thermodynamics of Thorium, Volume 11

Access the complete publication at:
<https://doi.org/10.1787/9789264056688-en>

Please cite this chapter as:

OECD/Nuclear Energy Agency (2008), "Thorium Group 14 compounds and complexes", in *Chemical Thermodynamics of Thorium, Volume 11*, OECD Publishing, Paris.

DOI: <https://doi.org/10.1787/9789264056688-12-en>

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