Appendix A

Discussion of selected references

This appendix comprises discussions relating to a number of key publications, which contain experimental information cited in this review. These discussions are fundamental in explaining the accuracy of the data concerned and the interpretation of the experiments, but they are too lengthy or are related to too many different sections to be included in the main text. The notation used in this appendix is consistent with that used in the present book, and not necessarily consistent with that used in the publication under discussion.

[1908WOH/PLU]

The decomposition pressures of a large number of metallic sulphates were determined manometrically, using a porcelain container. The rapid equilibration to form $SO_3(g)$ was ensured by the presence of a platinum wire in the reaction tube.

Two sets of measurements were carried out for $Th(SO_4)_2(s)$. One sample, prepared from pure thorium nitrate, was studied at temperatures from 848 to 1058 K; these measurements gave somewhat scattered results. A second run involved a partially decomposed thorium sulphate, which gave essentially similar decomposition values (from 796 to 1073 K), which were less scattered than in the first experiment. From the close similarity of the equilibrium pressures in the two runs, the authors concluded that no oxysulphate was stable in this temperature range. There also seems to be the possibility that in the first set of experiments, the sulphate decomposed rapidly during the initial heating, and both studies involved an oxysulphate phase.

However, using the selected heat capacities for $Th(SO_4)_2(cr)$, we have made a second-law calculation of their results, assuming the reaction is that postulated by the authors,

$$Th(SO_4)_2(cr) \rightleftharpoons ThO_2(cr) + 2SO_2(g) + O_2(g)$$

to derive the enthalpy of formation and entropy of $Th(SO_4)_2(cr)$. Unfortunately, the values obtained $\Delta_f H^\circ_m(Th(SO_4)_2, cr, 298.15\ K) = -2184.3\ kJ\cdot mol^{-1}$ and $S^\circ_m(Th(SO_4)_2, cr, 298.15\ K) = 453.7\ J\cdot K^{-1}\cdot mol^{-1}$ are not reasonable for $Th(SO_4)_2(cr)$. We thus conclude that the reaction studied was not that proposed by the authors, or some adventitious volatile material was present in their experiments for $Th(SO_4)_2(cr)$. This study has therefore not been considered further in the review.

[1910BAR]

See discussion in [1910KOP/HOL].

[1910KOP]

The enthalpies of solution of the tetrahydrate and the octahydrate of $Th(SO_4)_2$ were determined in *ca.* 1 M K_2CO_3 solution at *ca.* 15°C, to be $-(119.90 \pm 1.50)$ and $-(61.85 \pm 2.30)$ $kJ\cdot mol^{-1}$ respectively (statistical uncertainties only). If it is assumed that the (ill-defined) product formed by the reaction of the two hydrates is the same, and the small difference in temperature of the study from 298.15 K is ignored, the calorimetric data give for the hydration reaction:

$$Th(SO_4)_2\cdot 4H_2O(cr) + 4H_2O(l) \rightleftharpoons Th(SO_4)_2\cdot 8H_2O(cr) \qquad (A.1)$$

$$\Delta_r H_m^\circ((A.1), 298.15\ K) = -(58.0 \pm 5.0)\ kJ\cdot mol^{-1}$$

where the uncertainty has been estimated by the review.

The temperatures at which the two hydrates coexist with the aqueous phase were found to be 42°C in water, and 30°C in 33 wt% H_2SO_4, 19.5 wt% HCl, and 31 wt% HNO_3 solutions. The activities of water (a_w) at 30°C in the last three solutions are calculated to be 0.702, 0.623 and 0.712 respectively from the data in [1984HAR/MOL] for H_2SO_4 and [1991PIT] for HNO_3 and HCl. With the mean value of $a_w = (0.679 \pm 0.069)$, the enthalpy of Reaction (A.1) is calculated to be $-(102.5 \pm 28.4)$ $kJ\cdot mol^{-1}$, the large uncertainty emanating from a combination of the very short temperature range and the uncertainty in the water activity in the acidic solutions. The calorimetric value is clearly to be preferred, but no value can be selected.

[1910KOP/HOL]

The data from [1910KOP/HOL], [1910BAR], [1911BAR], [1912BAR], and [1912WIR] for different chemical systems are compiled in [1965LIN2] and were used to partially validate the thorium sulphate aqueous phase model selected in this review. No thermodynamic data are given in these publications, but the data they contain were useful in determining the $\Delta_f G_m^\circ$ values for the reported solid phases. For details of the aqueous phase model, including the associated ion interaction parameters and the auxiliary data used in these calculations, and for $\Delta_f G_m^\circ$ values of different solids determined from this modelling, see the main text. In fitting these data at different temperatures, the $\Delta_f G_m^\circ$ value of H_2O and the temperature corrected value of the Debye-Hückel term at the experimental temperatures were used. The graphical comparisons of the data are provided in figures included in the main text. The details of the experimental data listed in these publications and of the concentrations of predicted species are reported in the following tables. In a limited number of cases involving very high ionic strengths, where the SIT model is not applicable, no predictions were made and thus only the experimental concentrations are listed in these cases.

Table A-1: Observed [1912BAR] and model-predicted concentrations at 25°C for the solubility of $Th(SO_4)_2·9H_2O(cr)$ in Li_2SO_4 solutions (data plotted in Figure IX-5).

Experimental data (m)			Model predictions (m)				
Li^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
0.000	$8.120×10^{-2}$	$4.060×10^{-2}$	$3.522×10^{-2}$	$9.410×10^{-6}$	$5.988×10^{-3}$	$2.777×10^{-2}$	$1.449×10^{-3}$
$4.680×10^{-1}$	$4.288×10^{-1}$	$9.740×10^{-2}$	$9.203×10^{-2}$	$8.334×10^{-6}$	$1.844×10^{-3}$	$2.995×10^{-2}$	$6.023×10^{-2}$
$8.960×10^{-1}$	$7.400×10^{-1}$	$1.460×10^{-1}$	$1.535×10^{-1}$	$1.129×10^{-5}$	$1.739×10^{-3}$	$3.183×10^{-2}$	$1.199×10^{-1}$
1.270	1.011	$1.880×10^{-1}$	$2.110×10^{-1}$	$1.286×10^{-5}$	$1.685×10^{-3}$	$3.347×10^{-2}$	$1.758×10^{-1}$

Table A-2: Observed [1911BAR] and model-predicted concentrations at 16°C for the solubility of different thorium-sulphate solids in $(NH_4)_2SO_4$ solutions (data plotted in Figure IX-9).

Experimental data (m)			Model predictions (m)				
NH_4^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2·9H_2O(cr)$							
0.000	$6.560×10^{-2}$	$3.280×10^{-2}$	$3.280×10^{-2}$	$8.757×10^{-6}$	$5.651×10^{-3}$	$2.585×10^{-2}$	$1.294×10^{-3}$
$3.220×10^{-1}$	$3.196×10^{-1}$	$7.930×10^{-2}$	$6.498×10^{-2}$	$7.202×10^{-6}$	$1.885×10^{-3}$	$2.723×10^{-2}$	$3.586×10^{-2}$
$7.280×10^{-1}$	$6.120×10^{-1}$	$1.240×10^{-1}$	$1.122×10^{-1}$	$1.266×10^{-5}$	$1.889×10^{-3}$	$2.889×10^{-2}$	$8.138×10^{-2}$
1.520	1.181	$2.110×10^{-1}$	$2.168×10^{-1}$	$2.252×10^{-5}$	$2.054×10^{-3}$	$3.211×10^{-2}$	$1.826×10^{-1}$
2.500	1.878	$3.140×10^{-1}$	$3.843×10^{-1}$	$3.441×10^{-5}$	$2.319×10^{-3}$	$3.642×10^{-2}$	$3.455×10^{-1}$
$Th(SO_4)_2.(NH_4)_2SO_4.4H_2O(cr)$							
2.500	1.878	$3.140×10^{-1}$	$3.260×10^{-1}$	$2.439×10^{-5}$	$1.724×10^{-3}$	$2.873×10^{-2}$	$2.955×10^{-1}$
4.240	2.608	$2.440×10^{-1}$	$2.424×10^{-1}$	$5.871×10^{-6}$	$4.101×10^{-4}$	$9.004×10^{-3}$	$2.330×10^{-1}$
5.340	3.134	$2.320×10^{-1}$	$2.235×10^{-1}$	$2.932×10^{-6}$	$2.087×10^{-4}$	$5.236×10^{-3}$	$2.181×10^{-1}$
$Th(SO_4)_2.2(NH_4)_2SO_4.2H_2O(cr)$							
5.340	3.134	$2.320×10^{-1}$					
6.840	3.730	$1.550×10^{-1}$					
7.440	3.992	$1.360×10^{-1}$					
$Th(SO_4)_2.3(NH_4)_2SO_4.3H_2O(cr)$							
8.020	4.226	$1.080×10^{-1}$					
10.56	5.358	$3.900×10^{-3}$					

Table A-3: Observed [1910BAR] and [1911BAR] and model-predicted concentrations at 16°C for the solubility of different thorium-sulphate solids in Na_2SO_4 solutions (data plotted in Figure IX-7).

Experimental data (m)			Model predictions (m)				
Na^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2.9H_2O(cr)$ [a]							
1.540×10^{-1}	1.590×10^{-1}	4.100×10^{-2}	4.616×10^{-2}	4.865×10^{-6}	2.026×10^{-3}	2.659×10^{-2}	1.754×10^{-2}
2.760×10^{-1}	2.500×10^{-1}	5.600×10^{-2}	5.987×10^{-2}	6.566×10^{-6}	1.908×10^{-3}	2.712×10^{-2}	3.084×10^{-2}
4.200×10^{-1}	3.960×10^{-1}	9.300×10^{-2}	7.613×10^{-2}	8.558×10^{-6}	1.869×10^{-3}	2.763×10^{-2}	4.662×10^{-2}
$Th(SO_4)_2\cdot[Na_2SO_4]\cdot6H_2O(cr)$							
4.200×10^{-1}	3.960×10^{-1}	9.300×10^{-2}	1.185×10^{-1}	1.791×10^{-5}	3.225×10^{-3}	4.300×10^{-2}	7.227×10^{-2}
5.780×10^{-1}	4.490×10^{-1}	8.000×10^{-2}	8.260×10^{-2}	8.552×10^{-6}	1.543×10^{-3}	2.412×10^{-2}	5.693×10^{-2}
8.160×10^{-1}	5.080×10^{-1}	5.000×10^{-2}	5.192×10^{-2}	3.862×10^{-6}	6.197×10^{-4}	1.106×10^{-2}	4.024×10^{-2}
1.320	7.240×10^{-1}	3.300×10^{-2}	3.054×10^{-2}	1.728×10^{-6}	2.173×10^{-4}	4.238×10^{-3}	2.608×10^{-2}
1.720	9.180×10^{-1}	2.800×10^{-2}	2.390×10^{-2}	1.150×10^{-6}	1.258×10^{-4}	2.554×10^{-3}	2.122×10^{-2}
2.160	1.130	2.500×10^{-2}	1.983×10^{-2}	8.166×10^{-7}	7.982×10^{-5}	1.669×10^{-3}	1.808×10^{-2}

a: The data reported by [1910BAR] and [1911BAR] indicate that the solubility controlling phase in the entire set is $Th(SO_4)_2\cdot[Na_2SO_4]\cdot6H_2O(cr)$. However, thermodynamic modelling and plotting of the data clearly show that the solubility controlling phase in the first two samples is $Th(SO_4)_2\cdot9H_2O(cr)$ and that the third sample is in equilibrium with both $Th(SO_4)_2\cdot9H_2O(cr)$ and $Th(SO_4)_2\cdot[Na_2SO_4]\cdot6H_2O(cr)$.

Table A-4: Observed [1911BAR] and model-predicted concentrations at 16°C for the solubility of different thorium-sulphate solids in K_2SO_4 solutions (data plotted in Figure IX-8).

Experimental data (m)			Model predictions (m)				
K^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2 \cdot 9H_2O(cr)$ [a]							
4.860×10^{-2}	1.029×10^{-1}	3.930×10^{-2}	3.479×10^{-2}	3.635×10^{-6}	2.532×10^{-3}	2.607×10^{-2}	6.184×10^{-3}
1.150×10^{-1}	1.610×10^{-1}	5.170×10^{-2}	4.230×10^{-2}	3.955×10^{-6}	2.019×10^{-3}	2.636×10^{-2}	1.392×10^{-2}
$Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O(cr)$							
1.320×10^{-1}	2.167×10^{-1}	7.530×10^{-2}	7.385×10^{-2}	1.007×10^{-5}	4.024×10^{-3}	4.599×10^{-2}	2.383×10^{-2}
1.410×10^{-1}	1.889×10^{-1}	5.930×10^{-2}	5.877×10^{-2}	6.500×10^{-6}	2.772×10^{-3}	3.507×10^{-2}	2.092×10^{-2}
1.470×10^{-1}	1.785×10^{-1}	5.240×10^{-2}	5.206×10^{-2}	5.180×10^{-6}	2.265×10^{-3}	3.021×10^{-2}	1.958×10^{-2}
1.550×10^{-1}	1.578×10^{-1}	4.020×10^{-2}	4.230×10^{-2}	3.624×10^{-6}	1.624×10^{-3}	2.339×10^{-2}	1.728×10^{-2}
$Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O(cr)$							
1.582×10^{-1}	1.563×10^{-1}	3.860×10^{-2}	3.943×10^{-2}	3.234×10^{-6}	1.466×10^{-3}	2.155×10^{-2}	1.641×10^{-2}
1.708×10^{-1}	1.259×10^{-1}	2.050×10^{-2}	2.225×10^{-2}	1.422×10^{-6}	6.820×10^{-4}	1.128×10^{-2}	1.029×10^{-2}
2.118×10^{-1}	1.234×10^{-1}	8.730×10^{-3}	9.106×10^{-3}	4.665×10^{-7}	2.190×10^{-4}	4.066×10^{-3}	4.821×10^{-3}
3.550×10^{-1}	1.808×10^{-1}	1.650×10^{-3}	1.109×10^{-3}	4.635×10^{-8}	1.682×10^{-5}	3.569×10^{-4}	7.357×10^{-4}
$Th(SO_4)_2 \cdot 3.5K_2SO_4(cr)$							
4.640×10^{-1}	2.320×10^{-1}	6.360×10^{-4}	4.144×10^{-4}	1.607×10^{-8}	4.962×10^{-6}	1.102×10^{-4}	2.992×10^{-4}
5.540×10^{-1}	2.770×10^{-1}	7.080×10^{-5}	1.109×10^{-4}	4.020×10^{-9}	1.114×10^{-6}	2.555×10^{-5}	8.420×10^{-5}

[a] The data reported by [1911BAR] indicates that the solubility controlling phase in these two samples is $Th(SO_4)_2 \cdot K_2SO_4 \cdot 6H_2O$. However, modelling of these data suggests that the solubility controlling phase should be $Th(SO_4)_2 \cdot 9H_2O$.

Table A-5: Observed [1912BAR] and [1912WIR] and model-predicted concentrations at 25°C for the solubility of different thorium-sulphate solids in H_2SO_4 solutions (data plotted in Figure IX-6).

Experimental data (m)			Model predictions (m)				
H^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2\cdot9H_2O(cr)$							
0.000	8.200×10^{-2}	4.100×10^{-2}	3.515×10^{-2}	9.393×10^{-6}	5.979×10^{-3}	2.772×10^{-2}	1.445×10^{-3}
2.200×10^{-1}	2.000×10^{-1}	4.500×10^{-2}	4.072×10^{-2}	1.490×10^{-5}	4.396×10^{-3}	2.867×10^{-2}	7.636×10^{-3}
4.000×10^{-1}	2.940×10^{-1}	4.700×10^{-2}	4.508×10^{-2}	2.247×10^{-5}	4.840×10^{-3}	2.941×10^{-2}	1.081×10^{-2}
5.800×10^{-1}	3.870×10^{-1}	4.860×10^{-2}	4.900×10^{-2}	2.927×10^{-5}	5.282×10^{-3}	3.015×10^{-2}	1.354×10^{-2}
7.800×10^{-1}	4.870×10^{-1}	4.860×10^{-2}	5.310×10^{-2}	3.551×10^{-5}	5.743×10^{-3}	3.099×10^{-2}	1.633×10^{-2}
1.060	6.260×10^{-1}	4.800×10^{-2}	5.855×10^{-2}	4.189×10^{-5}	6.351×10^{-3}	3.217×10^{-2}	1.999×10^{-2}
1.640	9.080×10^{-1}	4.390×10^{-2}					
2.060	1.110	4.100×10^{-2}					
2.240	1.190	3.500×10^{-2}					
4.720	2.400	2.100×10^{-2}					
7.700	3.850	1.000×10^{-2}					
$Th(SO_4)_2\cdot8H_2O(cr)$							
12.10	6.050	2.500×10^{-3}					
14.14	7.070	1.500×10^{-3}					

Table A-6: Observed [1910KOP/HOL] and model-predicted concentrations at 30°C for the solubility of different thorium-sulphate solid in HCl solutions.

Experimental data (m)				Model predictions (m)				
H^+	Cl^-	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2\cdot8H_2O(cr)$								
0.000	0.000	1.014×10^{-1}	5.070×10^{-2}	2.343×10^{-2}	6.429×10^{-6}	4.327×10^{-3}	1.834×10^{-2}	7.550×10^{-4}
1.307	1.307	1.712×10^{-1}	8.560×10^{-2}	9.625×10^{-2}	1.529×10^{-2}	5.457×10^{-2}	2.468×10^{-2}	1.712×10^{-3}
2.048	2.048	1.686×10^{-1}	8.430×10^{-2}	1.207×10^{-1}	2.500×10^{-2}	6.489×10^{-2}	2.875×10^{-2}	2.080×10^{-3}
3.789	3.789	1.426×10^{-1}	7.130×10^{-2}					
5.110	5.110	1.228×10^{-1}	6.140×10^{-2}					
6.154	6.154	1.166×10^{-1}	5.830×10^{-2}					
$Th(SO_4)_2\cdot4H_2O(cr)$								
6.850	6.850	1.134×10^{-1}	5.670×10^{-2}					
6.850	6.850	1.150×10^{-1}	5.750×10^{-2}					
8.610	8.610	7.080×10^{-2}	3.540×10^{-2}					

[1911BAR]

See discussion in [1910KOP/HOL].

[1911CHA]

This early study is concerned with the preparation and the investigation of the properties of thorium metal and of a large number of compounds: oxide, hydroxide, various halides, oxyhalides, halogenocomplexes, their hydrates and adducts with ammonia. Elemental analyses were given for many of the compounds studied. Enthalpies of solution at 288 K of the metal in *ca.* 3.6 M HCl and of a number of compounds in *ca.* 16000 H_2O were reported. Values were given without any detail. Although the concentration of thorium in the calorimetric solutions was not specified in every case, it was assumed by this review to be the same throughout.

As the metal samples obtained in this study were reported to be only 92−96% pure, neither the enthalpy of solution of the metal nor its enthalpy of combustion to ThO_2(cr) will be considered further.

The enthalpy of solution of $ThCl_4$(cr) was given as −237.2 kJ·mol^{-1}. Using the values adopted in this review for $\log_{10}{}^{*}K^{\circ}_{s,0}$ ($Th(OH)_4$, am, 298.15 K) = (8.9 ± 1.1) (Section VII.4.1.1), for the equilibrium constants (Table VII-17) $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ ($Th_m(OH)_n^{4m-n}$, aq, 298.15 K), and for the value $\log_{10}{}^{*}\beta^{\circ}_{1}$ ($ThCl^{3+}$, 298.15 K) = (1.70 ± 0.10) listed in Section VIII.2.2.1, and assuming that the results of Chauvenet are valid for 298.15 K, the distribution of thorium in the various species in a *ca.* 16000 H_2O medium is calculated to be:

Th^{4+}	$Th(OH)^{3+}$	$Th(OH)_2^{2+}$	$Th_2(OH)_2^{6+}$	$Th_2(OH)_3^{5+}$	$Th_4(OH)_{12}^{4+}$	$ThCl^{3+}$
28.93%	46.02%	4.62%	0.02%	1.17%	0.08%	19.16%

These calculations are for an ideal aqueous solution, which will be a satisfactory approximation at the concentrations involved.

As no enthalpies of formation values have been selected by this review for the minor species $Th_2(OH)_3^{5+}$ and $Th_4(OH)_{12}^{4+}$, and since the presence of $Th_2(OH)_2^{6+}$ can be considered as negligible, we have assumed, for the evaluation of the result of Chauvenet, that the most hydrolysed species is $Th(OH)_2^{2+}$ and have included under this the other minor (1% or less) species.

Thus we assume the dissolution reaction of $ThCl_4$ to be:

$$\begin{aligned}&ThCl_4(cr) + 0.5780\ H_2O\ (\text{in } ca.\ 16000\ H_2O(l)) \rightleftharpoons\\&\quad(0.2893\ Th^{4+} + 0.4602\ Th(OH)^{3+} + 0.0589\ Th(OH)_2^{2+} +\\&\quad 0.1916\, ThCl^{3+} + 3.8084\, Cl^{-} + 0.5780\, H^{+})\ \text{in } ca.\, 16000\, H_2O(l)\qquad (A.2)\end{aligned}$$

To process Chauvenet's experimental value, we have therefore used the following auxiliary data: the enthalpy effect corresponding to the formation at infinite dilution of the various thorium hydrolytic species adopted in Table VII-15; $\Delta_f H_m$ (Th^{4+}, 298.15 K) = $-(768.7 \pm 2.3)$ kJ·mol^{-1}, assumed to be valid for the dilute medium used, and $\Delta_f H_m$ (Cl$^-$, *ca.* 4000 H$_2$O, 298.15 K) = $-(166.854 \pm 0.100)$ kJ·mol^{-1}. Also required is the enthalpy at infinite dilution of the reaction $\mathrm{Th^{4+} + Cl^- \rightleftharpoons ThCl_3^+}$, for which this review has not selected a value. However, [1968OHA/MOR] have suggested that this enthalpy effect is very small, and for the current comparison, we have used the value of (0.16 ± 2.00) kJ·mol^{-1} derived from the data given by [1982WAG/EVA], the uncertainty being conservatively estimated by this review. These values lead to $\Delta_f H_m^\circ$ (ThCl$_4$, cr, 298.15 K) = $-(1173.5 \pm 5.0)$ kJ·mol^{-1}, where the uncertainty does not include the unknown uncertainty of Chauvenet's determination. This value is to be compared with $\Delta_f H_m^\circ$ (ThCl$_4$, cr, 298.15 K) = $-(1186.3 \pm 1.3)$ kJ·mol^{-1} adopted in this review from more recent and better documented results. This may reveal a systematic difference between the results of Chauvenet and more recent data.

The enthalpies of solution in water of the thorium tetrachloride di-, tetra-, hepta-, and octahydrate were obtained as -171.88, -109.75, -61.5, and -47.91 kJ·mol^{-1}, respectively, under similar conditions to those for the anhydrous salt. With the logical assumption that the dissolution reaction was identical in all cases, the enthalpy of formation of these compounds can be obtained, from the comparison of their enthalpy of solution with that of the anhydrous salt obtained by Chauvenet, and $\Delta_f H_m^\circ$ (ThCl$_4$, cr, 298.15 K) = $-(1186.3 \pm 1.3)$ kJ·mol^{-1} selected in this review, using $\Delta_f H_m^\circ$ (H$_2$O, l, 298.15 K) = $-(285.830 \pm 0.040)$ kJ·mol^{-1}.

This yields $\Delta_f H_m^\circ$ (ThCl$_4$·2H$_2$O, cr, 298.15 K) = $-(1822.4 \pm 12.0)$ kJ·mol^{-1}, $\Delta_f H_m^\circ$ (ThCl$_4$·4H$_2$O, cr, 298.15 K) = $-(2456.2 \pm 12.0)$ kJ·mol^{-1} , $\Delta_f H_m^\circ$ (ThCl$_4$·7H$_2$O, cr, 298.15 K) = $-(3361.9 \pm 12.0)$ kJ·mol^{-1}, and $\Delta_f H_m^\circ$ (ThCl$_4$·8H$_2$O, cr, 298.15 K) = $-(3661.3 \pm 12.0)$ kJ·mol^{-1}, the large uncertainty limits being suggested by this review.

The enthalpy of solution of ThOCl$_2$(cr), ThOBr$_2$(cr), and ThOI$_2$(cr) in *ca.* 16000 H$_2$O were also reported as -117.78, -116.98, and -90.08 kJ·mol^{-1}, respectively. Use, as in the case of ThCl$_4$(cr) above, of the equilibrium constants for the hydrolysis of thorium, and, respectively, of $\log_{10} {}^*\beta_1^\circ$ (ThCl^{3+}, 298.15 K) = (1.70 ± 0.10) (Section VIII.2.2.1), $\log_{10} {}^*\beta_1^\circ$ (ThBr^{3+}, 298.15 K) = (1.37 ± 0.11) (Section VIII.3.2.1), and $\log_{10} {}^*\beta_1^\circ$ (ThI^{3+}, 298.15 K) = (1.25 ± 0.30) (Section VIII.4.2.1, based on the similar uranium species), allows the calculation of the distribution of thorium in the various species. This gives the approximate speciations given below.

$\mathrm{Th^{4+}}$	$\mathrm{Th(OH)^{3+}}$	$\mathrm{Th(OH)_2^{2+}}$	$\mathrm{Th_2(OH)_2^{6+}}$	$\mathrm{Th_2(OH)_3^{5+}}$	$\mathrm{Th_4(OH)_{12}^{4+}}$	Th(OH)$_4$(am) precipitate	$\mathrm{ThBr^{3+}}$
For the dissolution of ThOCl$_2$(cr)							
5.36%	25.90%	7.89%	0.01%	1.13%	55.98%	1.89%	
For the dissolution of ThOBr$_2$(cr)							
5.50%	26.39%	7.99%	0.01%	1.16%	57.39%	0.67%	0.89%
For the dissolution of ThOI$_2$(cr)							
5.67%	26.96%	8.09%	0.01%	1.20%	58.07%		

Compared to the case of the dissolution of the halides, the increased complexity of the hydrolysis phenomena and the appearance of small amounts of $Th(OH)_4$(am) precipitate in the case of the dissolution of the oxychloride and the oxybromide do not permit us to treat the data on the three oxyhalides with sufficient accuracy for any values to be selected.

For the enthalpy of solution of $ThBr_4$(cr), Chauvenet reported a value of – 293.67 kJ·mol^{-1}. Calculation yields the following distribution of thorium in the various species in the solution:

Th^{4+}	$Th(OH)^{3+}$	$Th(OH)_2^{2+}$	$Th_2(OH)_2^{6+}$	$Th_2(OH)_3^{5+}$	$Th_4(OH)_{12}^{4+}$	$ThBr^{3+}$
33.52%	49.82%	4.67%	0.02%	1.28%	0.07%	10.62%

Neglect, as in the case of the chloride, of three minor hydrolysis products yields a dissolution reaction that can be written as:

$$\begin{aligned}&ThBr_4(cr) + 0.6190\ H_2O\ (\text{in } ca.\ 16000\ H_2O(l)) \rightleftharpoons \\ &\quad (0.3352\,Th^{4+} + 0.4982\,Th(OH)^{3+} + 0.06040\,Th(OH)_2^{2+} + 0.1062\,ThBr^{3+} \\ &\quad + 3.8938\ Br^- + 0.6190\ H^+)\ \text{in } ca.\ 16000H_2O(l) \qquad (A.3)\end{aligned}$$

Use of the enthalpy of solution experimentally measured by Chauvenet (assumed to be valid at 298.15 K), $\Delta_{sol}H_m$ ($ThBr_4$, in *ca.*16000 H_2O, 298.15 K) = – 293.67 kJ·mol^{-1}, $\Delta_f H_m$ (Br^-, *ca.* 4000 H_2O, 298.15 K) = −(121.20 ± 0.15) kJ·mol^{-1}, and the same calculation procedure as for the dissolution of the tetrachloride (but neglecting the unknown, but likely to be negligible enthalpy effect, of the bromide complexation), leads to $\Delta_f H_m^\circ$ ($ThBr_4$, cr, 298.15 K) = −(932.6 ± 4.7) kJ·mol^{-1}, without consideration for the uncertainty in the experimental value reported by Chauvenet. This value is very distinctly less negative than that resulting from better documented more recent results adopted in this review, $\Delta_f H_m^\circ$ ($ThBr_4$, β, 298.15 K) = −(963.8 ± 2.0) kJ·mol^{-1}.

The enthalpies of solution in water of the thorium tetrabromide hepta-, deca- and dodecahydrate, respectively, were obtained as −94.35, −41.17, and −9.62 kJ·mol^{-1}, under similar conditions to those for the anhydrous salt. As in the case of the tetrachloride hydrates, the enthalpy of formation of these compounds can be obtained from the comparison of their enthalpy of solution with that of the anhydrous salt obtained by Chauvenet, and $\Delta_f H_m^\circ$ ($ThBr_4$, cr, 298.15 K) = −(963.8 ± 2.0) kJ·mol^{-1} selected in this review, using $\Delta_f H_m^\circ$ (H_2O, l, 298.15 K) = – (285.830 ± 0.040) kJ·mol^{-1}. This yields $\Delta_f H_m^\circ$ ($ThBr_4·7H_2O$, cr, 298.15 K) = −(3163.9 ± 12.0) kJ·mol^{-1}, $\Delta_f H_m^\circ$ ($ThBr_4·10H_2O$, cr, 298.15 K) = −(4074.6 ± 12.0) kJ·mol^{-1}, and $\Delta_f H_m^\circ$ ($ThBr_4·12H_2O$, cr, 298.15 K) = − (4677.8 ± 12.0) kJ·mol^{-1}, the large uncertainty limits being suggested by this review.

Chauvenet does not report any result on ThI_4(cr) but only mentions the difficulty in obtaining this compound in a pure state. In addition to his result on the enthalpy of solution of $ThOI_2$(cr) (see above), he reports as −41.97 kJ·mol^{-1} the enthalpy of solution in water of a compound analysed as $ThOI_2{\cdot}3.5H_2O$ (or $Th(OH)_2I_2{\cdot}2.5H_2O$) and as $-$ 35.31 kJ·mol^{-1}, the enthalpy of solution of a species reported as $Th(OH)I_3{\cdot}10H_2O$. As these compounds were not unambiguously characterised and, in view of the difficulty of ascertaining the dissolution processes, these values are given here for information only.

Enthalpies of solution of large number of ternary chlorides of thorium with alkali metals and ammonium and of their hydrates were also reported, as well as that of adducts of $ThCl_4$ with ammonia. These results are outside the bounds of the present review.

[1912BAR]

See discussion in [1910KOP/HOL].

[1912WIR]

See discussion in [1910KOP/HOL].

[1925BRI]

Britton [1925BRI] performed potentiometric titrations of 0.001, 0.002 and 0.01 M $Th(NO_3)_4$, 0.01 M $ThCl_4$ and 0.01 M $Th(SO_4)_2$ solutions with 0.1 M NaOH from pH 3 to pH 12 at 15°C. The 0.01 M $Th(NO_3)_4$ solution was also titrated with 0.1 M NH_4OH. The hydroxide solutions were added in about 20 steps (equilibration intervals of 5 to 15 minutes) and pH was calculated from the emf measured with a hydrogen electrode against a normal calomel reference electrode.

The onset of (visible) precipitation in these titrations was observed at pH 3.51 $-$ 3.60. This is in fair agreement with more recent solubility studies with ThO_2(am, hyd), *e.g.*, with [1963BIL/FUR] and [2002NEC/MUL] where the onset of precipitation / colloid formation in titrations at similar thorium concentrations was determined by light scattering or laser-induced breakdown detection.

The author noticed that less than four (3.24 $-$ 3.58) equivalents of alkali are required for neutrality (pH 7) during the titrations and concluded that the precipitates were "basic salts" containing certain amounts of nitrate, chloride or sulphate, *e.g.*, $Th(OH)_{3.43}(NO_3)_{0.57}$. This early paper provides only qualitative information, and no equilibrium constants can be derived from the experimental data reported in [1925BRI].

[1927PRE/HIN]

Manometric measurements of the pressure of CO(g) in from mixtures of ThO_2(cr) + graphite, heated in a graphite furnace, were made at eight temperatures from 2057 to 2494 K. The equilibrium pressures were determined by interpolating the rate of reaction (as measured by the rate of change of pressure) to zero. The results were fitted to the equation:

$$\log_{10} p_{\mathrm{CO}} / \mathrm{bar} = 8.075 - 19325\ T^{-1}.$$

Using the equivalent of a manual DTA apparatus, the melting point of "ThC_2" was found to be *ca*. 2773 K, appreciably below the assessed melting point from more recent determinations (2883 ± 35) K [1984HOL/RAN].

[1928BEC]

After a rather long discussion of electronic, structural and thermodynamics interrelationships between compounds of polyvalent elements, the author reports density measurements on various sulphates, halides, and binary and ternary oxides, and also enthalpies of reaction of such salts with solutions of different compositions.

Of direct interest to this review is the measurement of the enthalpy effect accompanying the reaction of $Th(SO_4)_2(cr)$ with a solution of NaOH.

The concentration of the dissolution medium was not specified and apparently, only one experiment was reported (0.8925 g $Th(SO_4)_2$ reacted with 500 cm^3 of solution). The lack of proper identity of the thorium hydroxide precipitate resulting from the reaction adds to the difficulty in extracting meaningful conclusions from this experiment. In a quite unclear way Beck [1928BEC] derives from his experimental result a value of $-483.3\ kJ{\cdot}mol^{-1}$ for the enthalpy of the reaction $ThO_2(cr) + 2SO_3 \rightleftharpoons Th(SO_4)_2(cr)$, at 291.15 K. The physical state of SO_3 to which this value applies is not stated, but is most probably gaseous.

With $\Delta_f H^\circ_m$ (SO_3, g, 298.15 K) = $-(395.9 \pm 0.7)\ kJ{\cdot}mol^{-1}$ from [1989GUR/VEY], and $\Delta_f H^\circ_m$ (SO_3, cr, 298.15 K) = $-(454.7 \pm 1.5)\ kJ{\cdot}mol^{-1}$, consistent with this value and the enthalpy of sublimation of $SO_3(cr)$, [1982WAG/EVA], this review obtains $\Delta_f H^\circ_m$ ($Th(SO_4)_2$, cr, 293.15 K) = -2502 or $-2560\ kJ{\cdot}mol^{-1}$, according as to whether the tabulated value refers to $SO_3(g)$ or $SO_3(cr)$. The small difference in temperature is neglected, as well as the enthalpy of hydration of $ThO_2(cr)$, so the uncertainties are unknown, but appreciable. These values are given for information only, given the lack of detail in the paper, and the ill-defined derivation of the value tabulated therein.

[1929FRI2]

Experimental data are reported for the vapour pressures at 0°C and 15°C of solutions of $Th(NO_3)_4$, (and other solutions) at five different water-to-thorium molar ratios ranging from 24.46 to 16.48 and for the enthalpies of dilution of six solutions ranging from initial water-to-thorium molar ratios of 15.65 to 28.18, to a final ratio of 510 to 562.

Experimental enthalpies of dilution were correlated with vapour pressures data, and the limits of such correlations in the case of thorium nitrate solutions were outlined.

[1930CHA/SOU]

These authors investigated the chemical and thermal stability of different thorium nitrate solids. They identified $Th(NO_3)_4{\cdot}5H_2O(cr)$ that formed as well defined crystals on slow evaporation at 15°C. The solid loses two molecules of water at 80°C and is transformed to $ThO(NO_3)_2\cdot0.5H_2O(cr)$ at 125°C. Further decomposition takes place at higher temperature. Heating under a gas phase composed of CO_2 and vapours from fuming nitric acid resulted in the formation of $Th(NO_3)_4\cdot2H_2O(cr)$ at 110°C. Solutions of the nitrate were titrated with NaOH and the reaction was followed by conductometry but no quantitative conclusions were drawn.

[1932NEU/KRO]

Neumann *et al.* [1932NEU/KRO] have measured the enthalpy of reaction of excess thorium (99% pure) with nitrogen at 298.15 K in an iron crucible in a bomb calorimeter. The overall N/Th of the reaction product was 0.69 − 0.87, but the main product was almost certainly $Th_3N_4(cr)$. From three experiments, these authors reported a value of $\Delta_f H_m$ (Th_3N_4, cr, 268.15 K) = $-(1290.3 \pm 16.3)$ kJ·mol^{-1}, their uncertainty limits being for the 2σ confidence level. Experiments on the combustion of unpurified thorium (95% pure) in nitrogen in a platinum crucible, presumably after correction for the lower Th content, gave slightly smaller enthalpies of reaction.

Since there is no indication in the publication that a correction was made to convert the value to constant pressure, this correction (− 16.0 kJ·mol^{-1} (Th_3N_4)) has been applied. The similar adjustment made by [1975RAN] seems to be too small by a factor of three. Thus this measurement gives $\Delta_f H_m^\circ$ (Th_3N_4, cr, 298.15 K) = $-(1306.3 \pm 16.3)$ kJ·mol^{-1} from this source. The uncertainties include those from the ill-defined composition of the product.

[1932ROT/BEC]

The enthalpies of formation of eight oxides (SiO_2, TiO_2, ZrO_2, HfO_2, ThO_2, GeO_2, Nb_2O_5, and Ga_2O_3) were determined at 293 K.

The thorium metal sample (reportedly “free of carbon”), obtained from J.H. de Boer (van Arkel and de Boer process, presumably [1925ARK/BOE], although this reference is not explicitly cited) was almost certainly much purer than previous preparations reported in the literature, especially with regard to light elements, although it contained 0.1% W.

A total of five oxygen combustion experiments, using two calibrated equipments were carried out, with concordant results and led to a value of $-(1224.2 \pm 5.8)$ kJ·mol^{-1} for the enthalpy of formation of $ThO_2(cr)$ at 293 K.

[1934JAE/VEE]

The heat capacities of metallic thorium (containing 6.04 mass% ThO_2) and ThO_2 were measured in what is assumed to be a drop calorimeter. Two samples of thorium were used: a rod, which was found to contain 6.04 mass% ThO_2, and a powder, found to contain 26.8 mass% ThO_2. Even after correction for the presence of thoria, the results for the powder were *ca.* 27% greater than those for the rod and were discounted by the authors.

The results were fitted to the expression (t / °C):

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th, cr}, t) = 7.97816 + 0.45997 \times 10^{-3}t + 0.10014 \times 10^{-5}t^2 + 0.10493 \times 10^{-8}t^3 \quad \mathrm{cal \cdot K^{-1} \cdot mol^{-1}}.$$

They agree reasonably well with more modern measurements using higher purity metal, but they were not included in the data fitting (see Section V.1.2)

The results for ThO_2 (671 − 1664 K) do not a have sensible variation with temperature, and have been discounted in view of the availability of more precise modern data.

[1934NEU/KRO]

The enthalpy of formation of Th_3N_4(cr) was determined from its enthalpy of combustion in 25 bar oxygen at 292 K in a bomb calorimeter. The compound was prepared by reacting 99% pure thorium metal filings with nitrogen as described in [1932NEU/KRO]. The measured weight gain corresponded to the formation of a material containing 99.03% Th_3N_4. The metal used in this study was the same as that used by the same group [1932NEU/KRO] for the direct determination of the heat of formation of Th_3N_4 from the elements.

Owing to the limited amount of material available, only one oxygen combustion could be realised. Analytical results showed that the combustion was close to 99% complete. For the reaction:

$$\mathrm{Th_3N_4(cr) + 3O_2(g) \rightleftharpoons 3ThO_2(cr) + 2N_2(g)} \qquad \text{(A.4)}$$

the authors reported a value (at constant volume) of − (2363.1 ± 4.6) kJ·mol^{-1}.

Correction of this value to constant pressure (for a net decrease of 1 mol gas), yields $\Delta_r H_m$((A.4), 292 K) = −(2371.1 ± 4.6) kJ·mol^{-1}. The value at 298.15 K is assumed to be the same.

The authors used the enthalpy of formation of ThO_2(cr) as determined by [1932ROT/BEC], in combination with their experimental result to obtain the enthalpy of formation of Th_3N_4(cr). Using $\Delta_f H^{\circ}_m$ (ThO_2, cr, 298.15 K) = −(1226.4 ± 3.5) kJ·mol^{-1} accepted in this review, and neglecting the small difference in temperature of the measurement of the enthalpy of combustion, we obtain $\Delta_f H^{\circ}_m$ (Th_3N_4, cr, 298.1 K) = − (1308.1 ± 11.5) kJ·mol^{-1}.

The authors also measured the enthalpies of formation of nine other oxides and nitrides. Their results are in reasonable accord with the current values selected by [1998CHA].

[1939FIS/GEW2]

A variant of the boiling point method for samples which attack silica was developed, and used to measure the vapour pressures of $ThCl_4$(cr) and $ThCl_4$(l), $ThBr_4$(cr) and $ThBr_4$(l) and ThI_4(l). Samples were contained in a molybdenum bell, immersed in liquid tin, and the pressure within the bell was balanced by argon on the outside.

$ThCl_4$(cr) and $ThBr_4$(cr) were prepared in a silica apparatus from a mixture of "pure" ThO_2 and sugar-charcoal with a stream of chlorine and sulphur chlorides, or bromine containing nitrogen. ThI_4(cr) was prepared from the elements. All samples were purified by sublimation, and were stated to give analyses agreeing with the theoretical values within the uncertainties. No details of the analyses are given.

The melting points of $ThCl_4$, $ThBr_4$ and ThI_4 were found to be (1043 ± 2) K, (952 ± 3) K and (839 ± 2) K respectively, and the vapour pressures to be represented by the following equations ($\log_{10} p/\text{bar} = \text{A}/T + \text{B}$) for the given temperature ranges.

Phase	Temperature range / K	A	B
$ThCl_4$(cr)	974 – 1036	– 12910	11.425
$ThCl_4$(l)	1052 – 1186	– 7587	6.695
$ThBr_4$(cr)	903 – 950	– 9628	8.855
$ThBr_4$(l)	955 – 1126	– 7549	6.685
ThI_4(l)	856 – 1107	– 6892	6.215

[1939SAT]

The mean specific heats of "Th_3N_4(cr)", Li_3N(cr), Zn_3N_2(cr) were measured with an ice calorimeter over three temperature intervals from 273.2 to 373.7 K, 578.9 K and 776.2 K. The sample of Th_3N_4(cr) was prepared from the elements, initially at 1013 K, and subsequently at 1113 K for six hours. Analyses showed that it contained 5.78 wt% N, 2.65 wt% O and 91.57 wt% Th. With current atomic weights, this corresponds to 77.59 wt% Th_3N_4(cr), 21.87 wt% ThO_2(cr) and 0.54 wt% Th(cr). As noted by Rand [1975RAN], the overall composition corresponds to a composition of $Th_2N_{2.09}O_{0.84}$, close to Th_2N_2O, and it is not clear whether the sample was a mixture of Th_3N_4(cr) and ThO_2(cr), as assumed by Sato, or Th_2N_2O(cr) and Th_3N_4(cr), or of all three phases, with or without reciprocal solubility. The following calculation assumes, with the author, the first possibility.

The three measurements of the mean specific heat were corrected by the review for these impurities, using the selected heat capacity data for ThO_2(cr), and Th(cr). The mean heat capacities of Th_3N_4(cr) are thus calculated to be: 164.96 $\text{J·K}^{-1}\text{·mol}^{-1}$ for 273.2−373.7 K; 178.80 for 273.2−578.9 K and 273.2−776.2 K. These are represented by the following equation for the true heat capacities:

$$[C^{\circ}_{p,\text{m}}]^{800\text{K}}_{273.2\text{K}}(\text{Th}_3\text{N}_4, \text{cr}, T) = 133.97 + 0.1142\,T + 5.983\times10^{5}\,T^{-2} \quad \text{J·K}^{-1}\text{·mol}^{-1}$$

giving

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th_3N_4, cr, 298.15\ K}) = 161.3\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

This is rather larger than the selected value $(147.7 \pm 8.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, and in view of the uncertainty in the phase composition of the sample, the data of [1939SAT] are not retained by this review.

[1941SOU]

Data are given for the heat content for thorium dioxide (to 1787 K). Impure thoria was purified from rare earths metals by dissolution in concentrated HCl and iodate precipitation, to give samples of 99.4% and 99.1% purity. No correction was made for the impurities. The samples were contained in a Pt-Rh cylinder and dropped into a copper block, whose temperature was monitored. The enthalpy increments were fitted to a four term extended Kelley equation from which the heat capacity was derived.

[1941STR/ZUM]

Strotzer and Zumbusch [1941STR/ZUM] have measured the sulphur decomposition pressures over a sample of composition $\mathrm{ThS_{2.19}}$ at four temperatures from 924 to 1027 K. Based on their structural and analytical studies, they took this to be a mixture of $\mathrm{ThS_2(cr)}$ and $\mathrm{Th_3S_7(cr)}$. However, we have preferred the interpretation of Graham and McTaggart [1960GRA/MCT] and assumed the higher sulphide to be $\mathrm{Th_2S_5(cr)}$. With corrections to the total pressure of sulphur vapour for the presence of $4-6\%$ higher sulphur polymers in the vapour (see Section IX.1.1.8), the results indicate that the enthalpy of formation of $\mathrm{Th_2S_5(cr)}$ is *ca.* $8.3\ \mathrm{kJ\cdot mol^{-1}}$ more negative than that of $\mathrm{ThS_2(cr)}$ around 1000 K.

[1944TOL]

Only an short abstract was available to the reviewers; the author uses UV spectra to suggest the formation of the species $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$, presumably in a solution with high carbonate concentration. It is not obvious to the reviewers how this assignment was made and this information has not been considered reliable.

[1947ROB/LEV]

The vapour pressures of aqueous solutions of $\mathrm{K_3Fe(CN)_6}$ and $\mathrm{Th(NO_3)_4}$ were determined by the isopiestic method. The osmotic and activity coefficients were determined from these data. Ions of high negative charges cause greater deviation from ideal behaviour than ions of high positive charge. It is postulated that this effect is due to the extensive hydration of the positive ions in contrast to the negative ions.

[1948MOE/SCH]

The paper describes an analytical method and does not provide any thermodynamic data.

[1948SOU]

Souchay has studied hydrolysis and the formation of polynuclear complexes of a number of different metal ions, including Th(IV), using cryoscopy. The method requires high total concentrations of the solute (in this case 0.4 M thorium nitrate) to which different amounts of NaOH were added. Souchay interpreted his result as the formation of a single tetranuclear complex $Th_4(OH)_8^{8+}$. There is no information on the pH in the system and as a result of later investigations discussed in the present review, it is well established that no single species can describe the hydrolysis of Th. There are no thermodynamic data reported and the data do not provide supporting evidence for the formation of a tetranuclear Th hydroxide complex.

[1949DOD/ROL]

The authors have studied the complex formation between Th(IV) and fluoride using the redox couple Fe(III)/Fe(II) as indicator electrode. In a separate experiment they determined the fluoride complexes formed by Fe^{3+} (the fluoride complex formation of Fe^{2+} is negligible under the conditions used). From the known equilibrium data for the iron system they then calculated the free fluoride concentration from the measured redox potential in test solutions that in addition to Fe(III)/Fe(II) also contained Th(IV); the indicator system acts as a fluoride selective electrode.

The experiments were made at 25.00°C in a $HClO_4$-$NaClO_4$ ionic medium with the ionic strength 0.50 M. The concentration of H^+ was varied in the different titrations and ranged from 0.03 to 0.30 M. All experimental details are carefully described.

The Fe(III)-F^- titrations were described with the following set of equilibrium constants for the reactions:

$$Fe^{3+} + HF(aq) \rightleftharpoons FeF^{2+} + H^+ \qquad {}^*K_1 = (189 \pm 5)$$

$$FeF^{2+} + HF(aq) \rightleftharpoons FeF_2^+ + H^+ \qquad {}^*K_2 = (10.4 \pm 0.4)$$

$$FeF_2^+ + HF(aq) \rightleftharpoons FeF_3(aq) + H^+ \qquad {}^*K_3 \approx 0.58$$

$$Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+ \qquad {}^*K_h$$

$$HF(aq) \rightleftharpoons H^+ + F^- \qquad K_4$$

$$HF(aq) + F^- \rightleftharpoons HF_2^- \qquad K_5$$

The equilibrium constants ${}^*K_h$, K_4 and K_5 taken from the literature are so small that they do not affect the values of the equilibrium constants ${}^*K_n$, $n = 1-3$. The latter are also in good agreement with previous studies discussed in [1949DOD/ROL].

The thorium experiments were made at a hydrogen ion concentration of approximately 0.05 M. The experimental $\bar{n}_F$ *vs.* $[F^-]$ curves had a break at $\bar{n}_F \approx 2$ where $ThF_4(s)$, presumably hydrated, was formed. The most accurate data were obtained in the range $1 < \bar{n}_F < 2$, which means that the equilibrium constant for the formation of ThF^{3+}

is somewhat less precise than that for the formation of $\mathrm{ThF_2^{2+}}$. Analysis of the data gave the following result:

$$\mathrm{Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+} \qquad {}^*K_1 = (4.5 \pm 0.5) \times 10^4$$

$$\mathrm{ThF^{3+} + HF(aq) \rightleftharpoons ThF_2^{2+} + H^+} \qquad {}^*K_2 = (650 \pm 15)$$

$$\mathrm{ThF_2^{2+} + HF(aq) \rightleftharpoons ThF_3^{+} + H^+} \qquad {}^*K_3 = (32 \pm 2)$$

The authors also used the test solutions where precipitation of $\mathrm{ThF_4(s)}$ occurred to determine the solubility constant, ${}^*K_s$, for the reaction:

$$\mathrm{ThF_4{\cdot}4H_2O(s) + 2H^+ \rightleftharpoons ThF_2^{2+} + 2HF(aq) + 4H_2O(l)} \qquad {}^*K_s = (5.9 \pm 0.5) \times 10^{-8}\ \mathrm{M}.$$

This is a precise experimental study and the equilibrium analysis made by the authors is accepted by this review.

[1949WES/ROB3]

The enthalpies of solution at 298.15 K of pure anhydrous $\mathrm{ThCl_4(cr)}$ in 1.000, 6.000, and 9.000 M HCl solutions were found to be − (240.25 ± 0.42), − (185.23 ± 0.42), and − (146.15 ± 0.42) $\mathrm{kJ{\cdot}mol^{-1}}$, respectively. The $\mathrm{ThCl_4}$ concentrations were approximately 0.005 M.

The $\mathrm{ThCl_4(cr)}$ used was purified by high-vacuum sublimation in quartz to eliminate oxychloride and loaded into the semi-microcalorimeter bulbs in a dry box. The sample used was of high purity as judged from the thorium and chlorine analyses which were given as 62.8% Th and 37.8% Cl (theoretical: 62.07% Th and 37.93% Cl) as determined by the analytical section of the authors' laboratory. No X-ray analysis was given, and the material is assumed to be the β polymorph normally obtained without long annealing at low temperatures. The presence of small amounts of the most likely impurity, $\mathrm{ThOCl_2}$, would have had a very small effect on the enthalpies of solution.

These data are used in the determination of $\Delta_\mathrm{f} H^\circ_\mathrm{m}$ ($\mathrm{Th^{4+}}$, 298.15 K) in conjunction with results from [1950EYR/WES], [1969SMI/THA], and [1973FUG/BRO].

[1950DAY/STO]

The authors have used a liquid-liquid extraction method with thenoyltrifluoroacetone (TTA) as the extracting ligand to study the complex formation between $\mathrm{Th^{4+}}$ and different organic and inorganic ligands. The characteristics of the experimental method are described in the main text of this review. The experiments have been made at 25°C using an aqueous phase with a constant hydrogen ion concentration and ionic strength of 0.50 M; the organic phase was 0.25 M TTA dissolved in benzene. Thorium was present in trace concentration, 10^{-6} M. The following ligands were investigated $\mathrm{Cl^-}$, $\mathrm{NO_3^-}$, $\mathrm{ClO_3^-}$, $\mathrm{BrO_3^-}$, $\mathrm{IO_3^-}$, $\mathrm{F^-}$, mono-, di- and tri-chloroacetate and formate. The total concentrations of the ligands were varied, while keeping [H^+] constant. The experimental equilibrium constants are given in Table A-7.

Table A-7: Equilibrium constants reported in [1950DAY/STO].

Reaction	Equilibrium constant
$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$	4.3×10^4
$Th^{4+} + 2HF(aq) \rightleftharpoons ThF^{3+} + 2H^+$	3.1×10^7
$Th^{4+} + IO_3^- \rightleftharpoons ThIO_3^{3+}$	7.6×10^2 M^{-1}
$Th^{4+} + 2\,IO_3^- \rightleftharpoons Th(IO_3)_2^{2+}$	6.2×10^4 M^{-2}
$Th^{4+} + 3\,IO_3^- \rightleftharpoons Th(IO_3)_3^+$	1.4×10^7 M^{-3}
$Th^{4+} + BrO_3^- \rightleftharpoons ThBrO_3^{3+}$	6.4 M^{-1}
$Th^{4+} + 2\,BrO_3^- \rightleftharpoons Th(BrO_3)_2^{2+}$	8.2 M^{-2}
$Th^{4+} + ClO_3^- \rightleftharpoons ThClO_3^{3+}$	1.84 M^{-1}
$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+}$	4.73 M^{-1}
$Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$	1.76 M^{-1}
$Th^{4+} + ClCH_2COOH \rightleftharpoons Th(ClCH_2COO)^{3+} + H^+$	1.33 M^{-1}
$Th^{4+} + Cl_2CHCOOH \rightleftharpoons Th(Cl_2CHCOO)^{3+} + H^+$	5.74 M^{-1}
$Th^{4+} + 2Cl_2CHCOOH \rightleftharpoons Th(Cl_2CHCOO)_2^{2+} + 2H^+$	12.7 M^{-2}
$Th^{4+} + Cl_3CCOOH \rightleftharpoons Th(Cl_3CCOO)^{3+} + H^+$	8.23 M^{-1}
$Th^{4+} + 2Cl_3CCOOH \rightleftharpoons Th(Cl_3CCOO)_2^{2+} + 2H^+$	26.7 M^{-2}

The fluoride complexes were also investigated in a nitrate ionic medium and the authors note that the distribution coefficients are lower than in a perchlorate medium, suggesting formation of a ternary complex $ThF(NO_3)^{2+}$. This review suggests that a more probable explanation is that the effect is due to changes in activity coefficients between the two media and therefore does not accept the suggestion of formation of ternary complexes. No equilibrium constant was determined for acetate and formate complexes because of indications of coextraction of a Th-TTA-acetate/formate complex, (so-called synergistic extraction).

The dissociation constants for tri- di- and mono-chloroacetic acids are 0.2, 0.05 and 0.0014 M, respectively. The experimental procedures and data analysis used in this study are satisfactory and the numerical values of the proposed equilibrium constants are therefore considered to be reliable, but are not selected since data on organic ligands are not included in the present review. However, the equilibrium constants for the weak complexes require extensive changes in the ionic medium and the observed variation in distribution coefficients could therefore also be a result of activity coefficient variations.

The authors have not made any error estimates of the constants, but this review estimates an uncertainty of ten percent in the constants accepted.

As discussed in previous volumes of this series it is difficult to distinguish between complex formation and activity factor variations in systems where weak complexes are formed, owing to the large changes in the composition of the ionic medium required to have a measurable effect in these systems. We will illustrate this point by a more detailed discussion of experimental data for the Th^{4+}-Cl^-, ClO_3^-, BrO_3^-, and NO_3^- systems, studied using liquid-liquid extraction with thenoyltrifluoroacetone (HL) as extractant; two different methods will be described. The experimental data are from [1950DAY/STO] and [1952WAG/STO].

The phase equilibrium is given by the reaction:

$$Th^{4+}(aq) + 4HL(org) \rightleftharpoons ThL_4(org) + 4H^+(aq) \tag{A.5}$$

and the equilibrium constant at $I = 0$ in both aqueous and organic phase is given by:

$$\begin{aligned}\log_{10} K^\circ = {} & \log_{10} [ThL_4(org)] - \log_{10} [Th^{4+}] + 4\log_{10} [H^+] - 4\log_{10} [HL(org)] \\ & + \log_{10} \gamma_{ThL_4(org)} - \log_{10} \gamma_{Th^{4+}} + 4\log_{10} \gamma_{H^+} - 4\log_{10} \gamma_{HL(org)}\end{aligned} \tag{A.6}$$

As thorium is usually a trace component and the composition of the organic phase and hence the activity coefficients of the organic species are constant (independent of the aqueous phase), Equation (A.6) can be rewritten as:

$$\log_{10}{}' K^\circ = \log_{10} [ThL_4(org)] - \log_{10} [Th^{4+}] + 4\log_{10} [H^+] - \log_{10} \gamma_{Th^{4+}} + 4\log_{10} \gamma_{H^+} \tag{A.7}$$

where $\log_{10}{}' K^\circ = \log_{10} K^\circ + 4\log_{10}[HL(org)] + 4 \log_{10} \gamma_{HL(org)} - \log_{10} \gamma_{ThL_4(org)}$ is the equilibrium constant for a given composition of the organic phase and $I = 0$ in the aqueous phase. Applying the SIT to mixed $HClO_4$-HX media, *e.g.*, for the data from [1950DAY/STO] at $I = 0.5$ M with $X^- = Cl^-$, ClO_3^-, BrO_3^-, and NO_3^-, Eq. (A.7) becomes:

$$\begin{aligned}\log_{10}{}' K^\circ = {} & \log_{10} [ThL_4(org)] - \log_{10} [Th^{4+}] + 4\log_{10} [H^+] + 16D \\ & + \{4\,\varepsilon(H^+, ClO_4^-) - \varepsilon(Th^{4+}, ClO_4^-)\}\, m_{ClO_4^-} + \{4\,\varepsilon(H^+, X^-) - \varepsilon(Th^{4+}, X^-)\}\, m_{X^-}\end{aligned} \tag{A.8}$$

The distribution coefficient D of thorium is defined by:

$$D = \frac{[Th]_{org}}{[Th]_{aq}} \tag{A.9}$$

where $[Th]_{org} = [ThL_4(org)]$ and $[Th]_{aq} = [Th^{4+}] + [ThX^{3+}] + [ThX_2^{2+}] + \ldots$ are the molar thorium concentrations in the organic and aqueous phase, respectively.

Method 1 (complexation model used in [1950DAY/STO] and [1952WAG/STO]). In a series of extraction experiments at constant H^+ concentration and constant ionic strength, *e.g.*, in $(H/Na)ClO_4$-$(H/Na)Cl$ mixtures with $I = [ClO_4^-] + [X^-]$, the changes in the measured distribution coefficients are interpreted as being due to the formation of ThX_n^{4-n} complexes:

$$Th^{4+} + nX^- \rightleftharpoons ThX_n^{4-n} \tag{A.10}$$

with

$$[\mathrm{Th}]_{\mathrm{aq}} = [\mathrm{Th}^{4+}] + \Sigma\,[\,\mathrm{ThX}_n^{4-n}\,] = [\mathrm{Th}^{4+}]\,(1 + \Sigma\,\beta_n [\mathrm{X}^-]^n) \qquad (A.11)$$

where β_n is the conditional formation constant of the complex ThX_n^{4-n} which is given by:

$$\beta_n = [\,\mathrm{ThX}_n^{4-n}\,]\,/\,[\mathrm{Th}^{4+}]\,[\mathrm{X}^-]^n \qquad (A.12)$$

Combination of Equations (A.9)−(A.12) yields the relation:

$$\frac{1}{D} = \frac{1}{D_{\mathrm{o}}}(1 + \sum \beta_n\ [\mathrm{X}^-]^n) \qquad (A.13)$$

where D_{o} is the distribution coefficient in pure perchlorate solution at (I = [ClO_4^-], [X^-] = 0). Equation (A.13) is then applied to calculate the conditional formation constants β_n. The constant ionic strength (I = [ClO_4^-] + [X^-]) is usually considered as sufficient to keep the activity coefficients of the aqueous species constant. However, as the distribution coefficient and thermodynamic equilibrium constant $\log_{10}{}'K^{\circ}$ are related by:

$$\begin{aligned}\log_{10}D + \log_{10}(1 + \sum \beta_n\ [\mathrm{X}^-]^n) &= \log_{10}{}'K^{\circ} - 16D - 4\log_{10}[\mathrm{H}^+]\\ &- \{4\,\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-)\}\,m_{\mathrm{ClO}_4^-} - \{4\,\varepsilon(\mathrm{H}^+,\mathrm{X}^-) - \varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)\}\,m_{\mathrm{X}^-}\end{aligned}$$

this complexation model implies the (incorrect) assumptions that $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-) = \varepsilon(\mathrm{H}^+,\mathrm{X}^-)$ and $\varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-) = \varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)$.

Method 2 (strict ion interaction model). In distinction to the complexation model, the ion interaction model takes into account the fact that the SIT coefficients $\varepsilon(\mathrm{M}^{z+},\mathrm{ClO}_4^-)$ differ from $\varepsilon(\mathrm{M}^{z+},\mathrm{X}^-)$ but ignores the formation of complexes ($[\mathrm{Th}]_{\mathrm{aq}} = [\mathrm{Th}^{4+}]$). The equations for $\log_{10}D$ (at $I_{\mathrm{m}} = m_{\mathrm{ClO}_4^-} + m_{\mathrm{X}^-}$) and $\log_{10}D_{\mathrm{o}}$ (at $m_{\mathrm{X}^-} = 0$ and $I_{\mathrm{m}} = m_{\mathrm{ClO}_4^-} + m_{\mathrm{X}^-} = (m_{\mathrm{ClO}_4^-})_{\mathrm{o}}$) are thus:

$$\begin{aligned}\log_{10}D = {}& \log_{10}{}'K^{\circ} - 16D - 4\log_{10} m_{\mathrm{H}^+} - \{4\,\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-)\}\,m_{\mathrm{ClO}_4^-}\\ & - \{4\,\varepsilon(\mathrm{H}^+,\mathrm{X}^-) - \varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)\}\,m_{\mathrm{X}^-}\end{aligned} \qquad (A.14)$$

and

$$\log_{10}D_{\mathrm{o}} = \log_{10}{}'K^{\circ} - 16D - 4\log_{10} m_{\mathrm{H}^+} - \{4\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) - \varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-)\}\,(m_{\mathrm{ClO}_4^-})_{\mathrm{o}} \qquad (A.15)$$

with

$$m_{\mathrm{ClO}_4^-} = (m_{\mathrm{ClO}_4^-})_{\mathrm{o}} - m_{\mathrm{X}^-} \qquad (A.16)$$

Combination of Eqs. (A.14)−(A.16) gives:

$$\begin{aligned}\log_{10} D = {}& \log_{10} D_{\mathrm{o}} - \{\varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^- - \varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)\}\,m_{\mathrm{X}^-}\\ & + 4\{\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) - \varepsilon(\mathrm{H}^+,\mathrm{X}^-)\}\,m_{\mathrm{X}^-}\end{aligned} \qquad (A.17)$$

Thus the solvent extraction data at constant ionic strength can be interpreted by taking into account only the changing composition of the $\mathrm{HClO_4}$-HX media. For the data from

[1950DAY/STO] at I = 0.5 M with Cl^-, ClO_3^-, BrO_3^- and NO_3^- and the known values of $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-) = (0.14 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$, Eq. (A.17) becomes:

$$\log_{10} D = \log_{10} D_{\mathrm{o}} - (0.14 \pm 0.13)\, m_{\mathrm{X}^-} + \{\varepsilon(\mathrm{Th}^{4+}, \mathrm{X}^-)\} - 4\varepsilon(\mathrm{H}^+, \mathrm{X}^-)\}\, m_{\mathrm{X}^-}. \qquad \text{(A.18)}$$

The values of $\{\varepsilon(\mathrm{Th}^{4+}, \mathrm{X}^-)\} - 4\varepsilon(\mathrm{H}^+, \mathrm{X}^-)\}$ obtained by linear regression, Figure A-1 to Figure A-4, are summarised in Table A-8 (last column) and compared to the values of $\{\varepsilon(\mathrm{Th}^{4+}, \mathrm{X}^-)\} - 4\varepsilon(\mathrm{H}^+, \mathrm{X}^-)\}$ that can be calculated from the known individual SIT coefficients (preceding column). The values for $\mathrm{X}^- = \mathrm{Cl}^-$ and ClO_3^- are in the expected range while the values for $\mathrm{X}^- = \mathrm{NO}_3^-$ and BrO_3^- are far outside the expected range. The results for the nitrate system are in strong contradiction to the TBP extraction study of [2006NEC/ALT] where the distribution coefficients could be described without nitrate complexes over a wide range of nitrate concentrations (0.05 − 3.0 M $\mathrm{NaNO_3}$ containing 0.01 − 0.02 M $\mathrm{HNO_3}$). The experimental data could be described by the activity coefficients calculated with the SIT and $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.31 \pm 0.12)\ \mathrm{kg{\cdot}mol^{-1}}$. On the other hand it is well known that nitrate complexes are formed by the tetravalent actinides as discussed in [1992GRE/FUG] and [2001LEM/FUG]. There is no evidence for coextraction of $\mathrm{HNO_3}$ or $\mathrm{HClO_4}$ in TTA-systems, which would change the activity of the species in the organic phase which are assumed to be constant. Coextraction is, however, known in TBP systems.

Table A-8: SIT coefficients obtained from linear regression (Figure A-1 to Figure A-4).

X	$\varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)$ [a] ($\mathrm{kg{\cdot}mol^{-1}}$)	$\varepsilon(\mathrm{H}^+,\mathrm{X}^-)$ [a] ($\mathrm{kg{\cdot}mol^{-1}}$)	$\{\varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-) - 4\,\varepsilon(\mathrm{H}^+,\mathrm{X}^-)\}$ ($\mathrm{kg{\cdot}mol^{-1}}$)	
ClO_4^-	0.70 ± 0.10 [b]	0.14 ± 0.02	0.14 ± 0.13	
Cl^-	0.25 ± 0.03	0.12 ± 0.01	− 0.23 ± 0.05	− 0.39 ± 0.14 [c]
ClO_3^-				− 0.41 ± 0.14 [c]
BrO_3^-				− 1.43 ± 0.14 [c]
NO_3^-	0.11 ± 0.02	0.07 ± 0.01	− 0.17 ± 0.05	− 0.91 ± 0.14 [c]
	0.31 ± 0.12 [b]	0.07 ± 0.01	0.03 ± 0.13	

a: From [1980CIA], [1992GRE/FUG], except otherwise stated.

b: Selected by this review, from [2006NEC/ALT].

c: $\{\varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)\} - 4\,\varepsilon(\mathrm{H}^+,\mathrm{X}^-)\}$ calculated from the results in [1950DAY/STO].

Figure A-1: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-HCl media at I = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of m_{Cl^-}

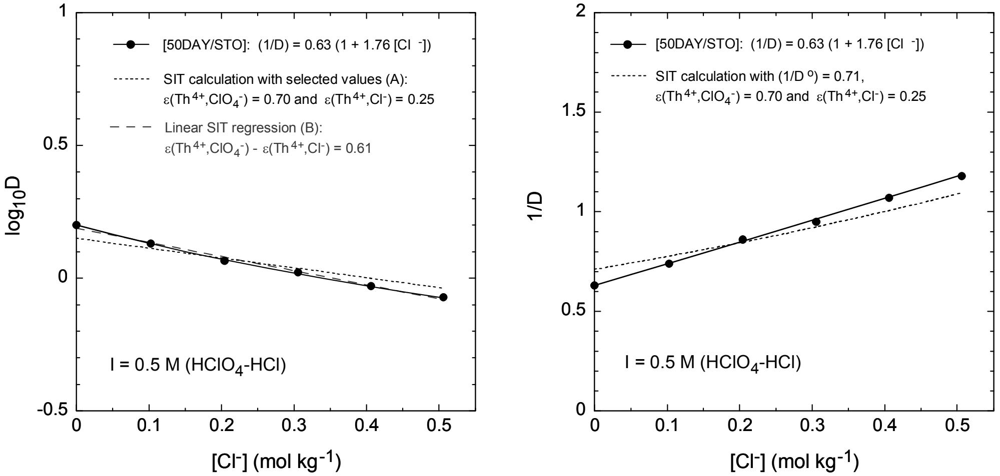


Figure A-2: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-$HClO_3$ media at I = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of $m_{ClO_3^-}$.

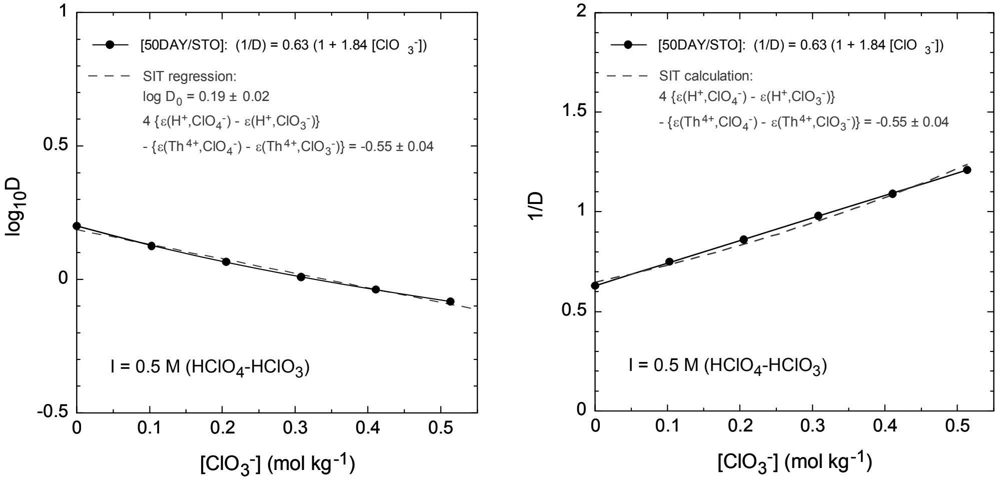


Figure A-3: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-$HBrO_3$ media at I = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of $m_{\mathrm{BrO}_3^-}$.

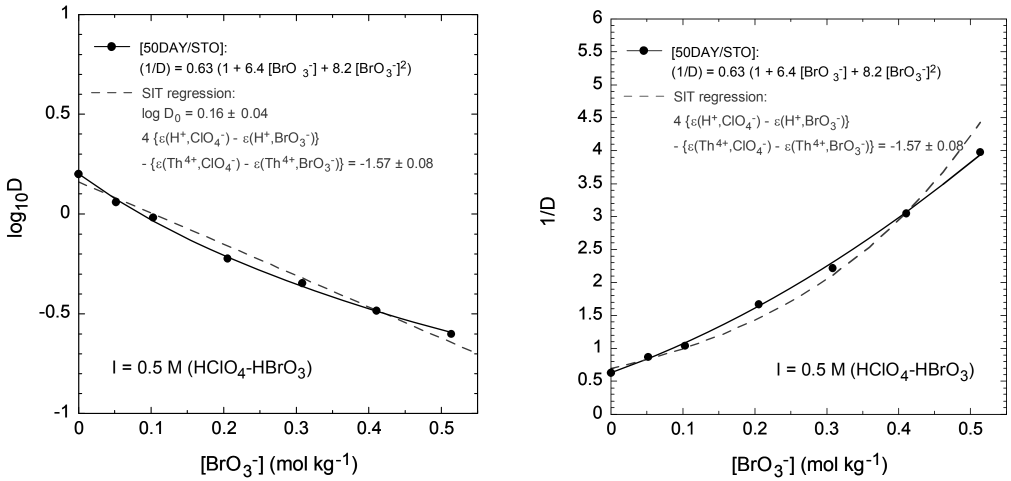
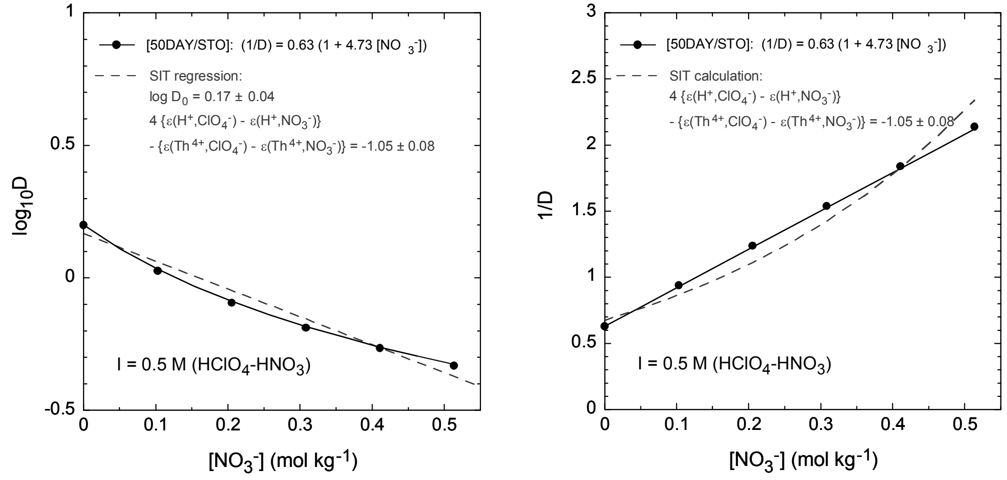


Figure A-4: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-HNO_3 media at I = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of $m_{\mathrm{NO}_3^-}$.



The same equilibrium system has also been studied using a nonlinear fitting code (NONLINT-SIT, described in Appendix D) with the experimental values of 1/*D* *vs.* [X^-], where *D* is the distribution coefficient between the organic and aqueous phases, fitted to determine the unknown interaction coefficients or the chemical potentials of the aqueous complexes. This approach took into account the changes in the chemical potential of the organic phase as a result of the changes in the Th content of the organic phase and used the code that included all of the appropriate SIT ion-interaction parameters to fit the data. This method has been used for both the data in [1950DAY/STO] and the more extensive data for the chloride system in [1952WAG/STO]; the results are given in Table A-9 and in more detail in the Appendix A entry for [1952WAG/STO]. The results in Table A-9 show that both methods provide similar best fitted values for $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$. The estimated $\varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_3^-)$ values based on linear regression (Figure A-2) and NONLINT-SIT (Figure VIII-10), 0.15 and 0.22 kg·mol^{-1} respectively, are also similar.

Table A-9: The $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ values based on reanalyses of literature data for the chloride system from [1950DAY/STO] and [1952WAG/STO] using linear regression and the NONLINT-SIT model.

Ionic strength (M)	Source of data	Best fit $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ (kg·mol^{-1})[a]	
		NONLINT-SIT	Linear regression
0.5	[1950DAY/STO]	0.20 ± 0.12	0.09 ± 0.04
0.5	[1952WAG/STO]	– 0.04 ± 0.16	– 0.09 ± 0.16
0.7	[1952WAG/STO]	0.08 ± 0.10	0.07 ± 0.10
1.0	[1952WAG/STO]	0.13 ± 0.16	0.15 ± 0.05
2.0	[1952WAG/STO]	0.23 ± 0.12	0.27 ± 0.02
4.0	[1952WAG/STO]	0.26 ± 0.22	0.32 ± 0.02
6.0	[1952WAG/STO]	0.25 ± 0.10	0.24 ± 0.02

a: NEA value for this parameter is (0.25 ± 0.03) kg·mol^{-1}.

Both methods show that when data for nitrate and bromate systems are interpreted based on only the changes in activity coefficients rather than the formation of aqueous complexes, the fitted $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-)$ and $\varepsilon(\mathrm{Th}^{4+},\mathrm{BrO}_3^-)$ values are too negative, suggesting that the interactions between Th^{4+} and NO_3^- or BrO_3^- must include the formation of complexes. The results from [1950DAY/STO] for the nitrate system are very different from those recently presented in [2006NEC/ALT] and are not appropriate for nitrate concentrations above 0.5 M and are not accepted by this review (see Section X.1.3.3 and [2006NEC/ALT] for further details).

The bromate data in [1950DAY/STO] when interpreted using NONLINT-SIT that included all of the appropriate ion interaction parameters to fit the $\Delta_\mathrm{f}G^\circ_\mathrm{m}/\mathrm{R}T$ value for ThBrO_3^{3+} showed that all the data can be fitted well (Figure VIII-12) with

$\Delta_f G^o_m / RT(\text{ThBrO}_3^{3+}) = -(280.981 \pm 0.066)$ ($\log_{10} \beta^o_1 = (1.897 \pm 0.028)$). This is contrary to the interpretations presented in [1950DAY/STO], which also included $\text{Th(BrO}_3)_2^{2+}$ species. This review finds no need to consider species other than ThBrO_3^{3+} when appropriate ion-interaction parameters (Table VIII-25) are included in the analysis and thus the $\text{Th(BrO}_3)_2^{2+}$ species should not be included in modelling this system with the selected values.

[1950EYR/WES]

This is an excellent study of the enthalpy of solution at 298.15 K of two samples of Th(cr) with 0.3 and 0.5 wt% impurities in 6.004 molar HCl containing 0.005 M Na_2SiF_6; the latter is required to avoid the formation of small amounts of insoluble residues. The average value obtained was −(760.2 ± 0.8) kJ·mol^{-1}. The enthalpy of solution of $ThCl_4$(cr) in the same medium was also measured to be −(186.52 ± 0.33) kJ·mol^{-1}, while a value of −(185.27 ± 0.25) kJ·mol^{-1} was reported for the dissolution in 6.004 M HCl in the absence of Na_2SiF_6.

The analytical data on the $ThCl_4$ were listed as 62.8% Th and 37.8% Cl as given by the manufacturers (theoretical: 62.07% Th and 37.93% Cl).

These results are used, in conjunction with the results of [1949WES/ROB3], [1969SMI/THA], and [1973FUG/BRO], to evaluate $\Delta_f H^o_m(\text{Th}^{4+})$ and $\Delta_f H^o_m(\text{ThCl}_4, \beta)$.

[1951MAL/CAM]

Dissociation pressures were measured in the Th-H system for the range of compositions up to *ca.* $ThH_{1.90}$ at temperatures from 924 to 1149 K. The thorium used contained about 0.2% impurities, chiefly oxygen (0.16%) and carbon (0.04%). In common with other investigators, the authors found that the dissociation pressure in the diphasic field {Th(cr) + ThH_{2-x}(cr)} increased with H/Th, possibly due to the effect of impurities or the failure to attain true equilibrium. The mean value of the enthalpy of solution from $ThH_{0.5}$(cr) to $ThH_{1.65}$(cr) in this temperature range was: −(143.5 ± 2.9) kJ·mol^{-1}, where, following [1984FLO/HAS], the uncertainty in this value has been increased from the authors' quoted value of 0.8 kJ·mol^{-1}. This corresponds to a value of −(148.1 ± 5.0) kJ·mol^{-1} at 298.15 K.

[1951ZEB/ALT]

The complex formation between Th(IV) and chloride, fluoride, nitrate, phosphate and sulphate has been studied using liquid-liquid extraction with thenoyltrifluoroacetone (TTA) as the extractant. The experiments have been made at 25°C at hydrogen ion concentrations sufficiently high (0.0875−2.00 M) to prevent hydrolysis of Th^{4+}. The chloride complexes have been studied in a medium of constant ionic strength 4.00 M using mixtures of $NaClO_4$ and NaCl at $[H^+] = 0.100$ M. The nitrate complexes have been studied in a mixture of $NaNO_3$ and $NaClO_4$ at $[H^+] = 0.075$ M and $I = 5.97$ M. The sulphate complexes were studied in a mixture of $NaHSO_4$, $NaClO_4$ and $HClO_4$ at $[H^+] = 0.500$, 1.00 and 1.99 M and ionic strength 2.00 M. The phosphate complexes were studied at varying concentrations of phosphoric acid in a mixture of $HClO_4$ and $NaClO_4$ ($[H^+]$ = 0.25, 0.50, 1.00 and 2.00 M) at ionic strength 2.00 M. The fluoride complexes were studied under the same conditions as used by Dodgen and Rollefson [1949DOD/ROL]. The experimental methods are described in detail and the distribution coefficient of TTA at different hydrogen ion concentrations has been determined. The authors have also tested the stoichiometry of the extracted Th-TTA complex and confirmed that it is $Th(TTA)_4$. The fluoride study gives equilibrium constants $K(A.19) = 5.0\times10^4$ and $K(A.20) = 2.9\times10^7$ that are in good agreement with those reported in [1949DOD/ROL] for the reactions:

$$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+ \qquad (A.19)$$

$$Th^{4+} + 2HF(aq) \rightleftharpoons ThF_2^{2+} + 2H^+ \qquad (A.20)$$

These constants have been accepted by this review; however, Zebroski *et al.* do not report uncertainty estimates and this review has therefore assigned an uncertainty of 10% to the constants.

The chloride and nitrate complexes are weak and it is then very difficult, or impossible, to decide if the variation in the measured distribution coefficients are due to complex formation or variation in activity coefficients. Zebroski *et al.* [1951ZEB/ALT] have described the distribution coefficient in the chloride system using four different complexes $ThCl_n^{4-n}$, with equilibrium constants $K_1 = 1.30$; $K_2 = 0.12$; $K_3 = 0.037$; $K_4 = 0.014$; this review considers these constants as fitting parameters and they are therefore not accepted. Zebroski *et al.* [1951ZEB/ALT] report the formation of two nitrate complexes $Th(NO_3)^{3+}$ and $Th(NO_3)_2^{2+}$ up to the highest nitrate concentration 4.93 M; their equilibrium constants are 2.83 and 1.91, respectively. This review does not accept these constants because of the high ionic strength and the large changes in the ionic medium in this study.

The sulphate system was described using the equilibria:

$$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+ \qquad (A.21)$$

$$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+ \qquad (A.22)$$

The equilibrium constants are $K(A.21) = 159$ and $K(A.22) = 2850$. The experimental distribution coefficients for the experiments at $[H^+] = 1.99$ M fall somewhat above the calculated distribution curve obtained using the data at $[H^+] = 0.50$ and 1.00 M. Zebroski *et al.* suggested that this was due to the formation of the complex $Th(SO_4)(HSO_4)^+$ with the equilibrium constant $K(A.23) = 800\ M^{-1}$ for the reaction:

$$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)(HSO_4)^+ + H^+ \qquad (A.23)$$

This constant has not been accepted by this review, as the complex was not confirmed in [1959ZIE]; in addition the substantial change in the ionic media at the different H^+ values might also result in ionic medium dependent distribution coefficients. The equilibrium constants K(A.21) = 159 and K_2(A.22) = 2850 are accepted by this review; the equilibrium constants for the reactions:

$$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+} \quad (A.24)$$

$$Th^{4+} + 2\,SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq) \quad (A.25)$$

calculated using the experimentally determined dissociation constant for HSO_4^-, K = 0.084 M, are β(A.24) = $(1.89 \pm 0.20)\times 10^3$ M^{-1}, and β(A.25) = $(4.04 \pm 0.4)\times 10^5$ M^{-2}. These constants are accepted by this review that has also estimated the uncertainty.

The phosphate system has been described using the equilibria:

$$Th^{4+} + H_3PO_4 \rightleftharpoons Th(H_3PO_4)^{4+} \qquad K = 78\ M^{-1} \quad (A.26)$$

$$Th^{4+} + H_3PO_4 \rightleftharpoons Th(H_2PO_4)^{3+} + H^+ \qquad K = 150 \quad (A.27)$$

$$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(H_2PO_4)(H_3PO_4)^{3+} + H^+ \qquad K = 1.4\times 10^4\ M^{-1} \quad (A.28)$$

$$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(H_2PO_4)_2^{2+} + 2H^+ \qquad K = 8.0\times 10^3 \quad (A.29)$$

This set of equilibrium constants describes the experimental data very well, but as pointed out by Zebroski *et al.* this is not sufficient proof to exclude the formation of species like $Th(HPO_4)^{2+}$ and $Th(H_3PO_4)_2^{4+}$. The previous NEA reviews on uranium, [1992GRE/FUG], neptunium and plutonium, [2001LEM/FUG] and [2003GUI/FAN] have not selected any equilibrium constants for M(IV) phosphate complexes; Zebroski *et al.* [1951ZEB/ALT] give all necessary experimental details and also a detailed analysis of the experimental data and this study is therefore accepted by this review.

[1952EYE/SEL]

This paper reports an extensive study of the Th-Se system. From thermal, metallographic, X-ray, and chemical analyses, four phases were identified in this binary system: ThSe(cr), which exists over a narrow solid-solution range; Th_2Se_3(cr), which has again a narrow solid-solution range; Th_7Se_{12}(cr); $ThSe_2$(cr), which loses Se when heated above 1273 K, being degraded to $ThSe_{1.7}$(cr). On the basis of X-ray powder diffraction data, the structure of the compounds could be identified and lattice parameters were given. Similarities and differences with the other thorium and actinide chalcogenides were discussed.

A tentative phase diagram was given for compositions from Th to $ThSe_{1.7}$. Above $ThSe_2$(cr), a further compound Th_3Se_7(cr) was reported but its structure could not be identified.

The ternary compound ThOSe(cr) was found as a contaminant in the system, most probably arising from the 0.5% oxygen contamination in the thorium metal used. ThOSe(cr) was also prepared by heating an equimolar mixture of ThO_2(cr) and

$ThSe_2$(cr) *in vacuo* at 1223 K. ThOSe(cr) was found to be isomorphous with thorium and uranium oxysulphides.

[1952HUB/HOL]

Precise measurements of the heats of combustion of thorium and uranium metals, and of uranium dioxide have been made and the enthalpies of formation of ThO_2(cr), UO_2(cr) and U_3O_8(cr) have been calculated.

A bomb calorimeter operating under 25 atm O_2 pressure was used for these determinations. The energy equivalent of the instrument had been determined using the combustion of benzoic acid. The details of the method and apparatus had been previously described. The thorium metal was in the form of 0.025 cm sheet and strands of 0.012 cm wire were used as fuse wire. Analysis of a portion the sheet showed that it contained 0.12% oxygen, 0.01% carbon, less than 0.01% iron and beryllium and no other metallic impurities in significant amounts.

The metal was burnt on sintered ThO_2 discs supported on a platinum platform. A total of 16 runs were made using samples ranging between 1.90 and 2.97 g in mass. Completeness of the combustion, which ranged between 99.74 and 99.99%, was determined by treating the combustion products with HCl and measuring the amount of hydrogen evolved. As it is well known that thorium metal leaves a residue upon dissolution in HCl, an empirical correction factor was determined from the gas evolved in the reaction of acid with weighed thorium metal samples. In the correction of the combustion results for the impurities contained in the metal, it was assumed that oxygen was present as ThO_2 and that the other impurities were present in the elemental form, neglecting the enthalpy of formation of carbides and alloys. After correction from the experimental temperature of 297.35 to 298.15 K, accounting for the deviation of oxygen from an ideal gas behaviour and converting from ΔE to $\Delta_f H_m$, the standard enthalpy of formation of formation of ThO_2 at 298.15 K was reported as $-(1226.9 \pm 1.5)$ kJ·mol^{-1}. Use of contemporary atomic masses leads to a value of $-(1226.4 \pm 1.5)$ kJ·mol^{-1}.

This value was adopted by CODATA [1989COX/WAG] with uncertainty limits increased to ± 3.5 kJ·mol^{-1}.

[1952MOE/QUI]

The authors describe the synthesis of $Th_2P_2O_6$ and have measured the solubility in HCl; the solubility in 1 M hydrochloric acid is 2.5×10^{-5} M demonstrating that the phase is sparingly soluble. There are no other thermodynamic data in this study.

[1952NOT/WIL]

Dissociation pressures were measured in the thorium-hydrogen system, as a function of composition, from *ca.* 573 to *ca.* 1073 K, and the structures of the two compounds formed, ThH_2(cr) and $ThH_{3.75 \pm x}$(cr) were studied by X-ray diffraction. Since this work was carried out some years before the publication date, the thorium metal used was not of the highest quality. Dissolution measurements showed that it certainly contained some combined thorium, probably ThO_2(cr), since the metal was cast in a BeO crucible. The metal used also contained *ca.* 0.03 wt% Zn, since it had been purified by alloying with zinc, followed by decomposition at 1873 K.

The structure of ThH_2 was indexed as a pseudotetragonal body-centred cell, ZrH_2 type with a = (4.09 ± 0.03) Å, c = (5.02 ± 0.03) Å. Most modern references describe this structure with a face-centred cell, for which the equivalent a parameter would be a = (5.78 ± 0.04) Å. The higher hydride was cubic, as indicated by [1953ZAC]. The lattice parameter increases with H/Th ratio, from (9.10 ± 0.02) Å for $ThH_{2.49}$ to (9.15 ± 0.02) Å for compositions approaching $ThH_{3.75}$.

In the dissociation pressure measurements, equilibrium was approached from both sides. Pressures were measured either manometrically or with a McLeod gauge. Steady pressures were attained in 5 to 10 minutes in the Th-ThH_2 system, but only after 1 to 5 hours when the higher hydride was involved (longer at 573 K), and even so the pressures from the decomposition side were very much larger than those from the absorption side. For both systems, the pressures in the "diphasic" region increased with H/Th ratio, indicating that impurities are playing a role in the "equilibria". The following equations (converted from those reported in torr) for the decomposition pressures, (calculated from the relatively flat region of the individual) isotherms as a function of temperature: Th-ThH_2, $\log_{10} p/\text{bar} = -7700/T + 6.665$, ThH_2-$ThH_{3.75}$: $\log_{10} p/\text{bar} = -4220/T + 6.625$. These data form the basis of the selected values for the enthalpies of formation of $ThH_{3.75}$(cr).

[1952SHA]

This was the first serious study of the vapour pressure of thoria. Weighed tungsten filaments coated with thoria were in heated *in vacuo* for a known period and the resultant mass loss determined directly. The brightness temperature of the filament was measured pyrometrically, and corrected to true temperature from a calibration curve obtained from another thoria-coated filament to which a Mo-W thermocouple was welded. Similar measurements were made using a molybdenum filament, with results indistinguishable from those from tungsten filaments.

Thirteen measurements were made from *ca.* 2060 to 2250 K, and the derived vapour pressures, assumed to be due to ThO_2(g) only, were given by the equation equivalent to $\log_{10} p/\text{bar} = -37100/T + 8.655$. Although it is now known that there is also an appreciable proportion of ThO(g) and O(g) in the vapour, as well as the predominant ThO_2(g), the major source of error was in the temperature measurements. The author found it difficult to get pyrometer readings reproducible to better than ± 20 K, especially at the higher temperatures; the corrections from brightness to true temperatures must also be somewhat uncertain. Nevertheless, these results agree well with the corpus of later, better defined, experiments.

[1952WAG/STO]

This is a careful experimental study wherein all details necessary for analysis of the experimental data are reported. Waggener and Stoughton have determined the complex formation in the Th^{4+}-Cl^- system using liquid-liquid extraction with TTA (thenoyltrifluoroacetone) as the extracting ligand and benzene as the organic solvent. The concentration of thorium is at the trace level and the experiments were made at 25°C at six different ionic strengths; the composition of the test solutions is shown in Table A-10. The total anion concentration of $[Cl^-] + [ClO_4^-]$ is equal to the ionic strength.

Table A-10: Compositions of test solutions.

Ionic strength (M)	$[H^+]$ (M)	$[Cl^-]$ concentration range (M)	$[Na^+]$ concentration range (M)
0.50	0.20	0.00 – 0.50	0.30 – 0.00
0.70	0.20	0.00 – 0.50	0.50 – 0.00
1.00	0.20	0.00 – 1.00	0.80 – 0.00
2.00	0.20	0.00 – 2.00	1.80
4.00	0.32	0.00 – 4.00	3.68
6.00	0.32	0.00 – 2.00	5.68

The experimental data were analysed by Waggener and Stoughton using a chloride complex model and their reported equilibrium constants are given in Table A-11.

Table A-11: Values of equilibrium constants reported by [1952WAG/STO].

Ionic strength (M)	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})
0.50	2.24	–	–	–
0.70	1.78	–	–	–
1.00	1.53	–	–	–
2.00	1.21	0.10	0.20	–
4.00	1.70	0.14	0.10	0.018
6.00	2.10	0.55	0.35	–

The authors do not report any uncertainty in the equilibrium constants; this review estimates the uncertainty in β_1 to at least 10% based on the uncertainty in the measured distribution coefficients. Waggener and Stoughton note the close agreement between their data and those in [1951ZEB/ALT] at the ionic strength 4.00 M; this is a good indicator for the experimental accuracy in both of these studies. In previous reviews it has been repeatedly pointed out that it is not possible to distinguish between complex formation and activity factor variations when analysing solution chemical data obtained with “standard” solution chemical methods (liquid-liquid distribution, ion-exchange, potentiometry *etc.*). This review has therefore reinterpreted the data of Waggener and Stoughton assuming that the experimental variations are due to activity factor variations when perchlorate is replaced by chloride. Two slightly different approaches that used the SIT ion-interaction theory were utilised and are discussed in detail under the Appendix entry for [1950DAY/STO]. The activity factor variations have been estimated using the SIT model with interaction coefficients given in Table A-12. The final results based on best fits to these data with both of these methods are summarised under [1950DAY/STO] and show that both approaches provide similar results. Therefore, the detailed analyses done with only one of these approaches (NONLINT-SIT) are presented in the tables and figures that follow. The tables list the experimental data extracted from [1952WAG/STO], including concentrations of thorium in the organic ($\mathrm{Th_{org}}$) and the aqueous ($\mathrm{Th_{aq}}$) and other constituents important in calculations, and predicted concentrations when a best fitted value of $\varepsilon(\mathrm{Th^{4+}, Cl^-})$ from the data is used in calculations. The figures show the comparison of experimental and predicted concentrations of Th(aq) or $1/D$, where D is the distribution coefficient of Th(IV) between the aqueous and organic phases, as a function of the molality of chloride concentrations when $\varepsilon(\mathrm{Th^{4+}, Cl^-}) = 0.25\ \mathrm{kg{\cdot}mol^{-1}}$ or that best fitted to the data are used.

Table A-12: SIT ion-interaction parameters and dimensionless molar Gibbs free energies of formation of species used in interpreting [1952WAG/STO] data for the estimation of activity factors in the $\mathrm{Th^{4+}}$-$\mathrm{Cl^-}$ system.

Species	ε ($\mathrm{kg{\cdot}mol^{-1}}$)	References
$\mathrm{H^+}$-$\mathrm{Cl^-}$	0.12 ± 0.01	Appendix B
$\mathrm{H^+}$- $\mathrm{ClO_4^-}$	0.14 ± 0.02	Appendix B
$\mathrm{Th^{4+}}$-$\mathrm{Cl^-}$	0.25 ± 0.03	Appendix B [a]
$\mathrm{Th^{4+}}$- $\mathrm{ClO_4^-}$	0.70 ± 0.10	This review, Section VI.3.1
$\mathrm{Na^+}$-$\mathrm{Cl^-}$	0.03 ± 0.01	Appendix B
$\mathrm{Na^+}$- $\mathrm{ClO_4^-}$	0.01 ± 0.01	Appendix B
$\mathrm{Na^+}$-$\mathrm{OH^-}$	0.04 ± 0.01	Appendix B
	$\Delta_\mathrm{f} G^\circ_\mathrm{m} / \mathrm{R}T$	
$\mathrm{Th^{4+}}$	$-\,284.305$	This review [b]

a: Predictions for [1952WAG/STO] data were made with $\varepsilon(\mathrm{Th^{4+}, Cl^-}) = 0.25\ \mathrm{kg{\cdot}mol^{-1}}$ or a value fitted with NONLINT-SIT for different ionic strengths. The best fitted $\varepsilon(\mathrm{Th^{4+}, Cl^-})$ values for I_c equal to 0.5, 0.7, 1.0, 2.0, 4.0, and 6.0 M are $-(0.04 \pm 0.16)$, (0.08 ± 0.10), (0.13 ± 0.16), (0.23 ± 0.12), (0.26 ± 0.22), $(0.25 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$, respectively.

b: $\Delta_\mathrm{f} G^\circ_\mathrm{m} / \mathrm{R}T$ values for other species ($\mathrm{H_2O, Na^+, Cl^-, ClO_4^-}$ and $\mathrm{OH^-}$) included in modelling were calculated from the values in Table IV-1.

- *SIT modelling calculation for thorium chloride system:*

Table A-13: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 0.5 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-) = -(0.04 \pm 0.16)\ \mathrm{kg{\cdot}mol^{-1}}$ and the other thermodynamic data listed in Table A-12. Selected data from this table are plotted in Figure A-5.

		Experimental [1952WAG/STO], I_c = 0.5 M						Predicted				
		Concentrations (m)						Concentrations (m)				
m/c^a	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.027	0.205	7.551	2.719	0.3081	0.00	0.5135	0.36	0.44	0.205	3.131	0.00352	0.787
1.027	0.205	7.496	2.774	0.3081	0.00	0.5135	0.37	0.43	0.205	3.108	0.00352	0.787
1.027	0.205	7.442	2.828	0.3081	0.00	0.5135	0.38	0.43	0.205	3.085	0.00352	0.787
1.027	0.205	7.415	2.855	0.3081	0.00	0.5135	0.39	0.43	0.205	3.074	0.00352	0.787
1.025	0.205	7.348	2.902	0.3075	0.05125	0.4613	0.40	0.47	0.205	3.260	0.00323	0.785
1.025	0.205	7.295	2.955	0.3075	0.05125	0.4613	0.41	0.46	0.205	3.236	0.00323	0.785
1.024	0.205	7.186	3.054	0.3072	0.1024	0.4096	0.43	0.50	0.205	3.427	0.00297	0.783
1.024	0.205	7.121	3.119	0.3072	0.1024	0.4096	0.44	0.50	0.205	3.396	0.00297	0.783
1.023	0.205	6.766	3.464	0.3069	0.1535	0.3581	0.51	0.51	0.205	3.469	0.00272	0.781
1.023	0.205	6.717	3.513	0.3069	0.1535	0.3581	0.52	0.51	0.205	3.444	0.00272	0.781
1.023	0.205	6.643	3.587	0.3069	0.1535	0.3581	0.54	0.50	0.205	3.406	0.00272	0.781
1.021	0.204	6.748	3.462	0.3063	0.2042	0.3063	0.51	0.57	0.204	3.698	0.00250	0.780
1.021	0.204	6.717	3.493	0.3063	0.2042	0.3063	0.52	0.56	0.204	3.681	0.00250	0.780
1.021	0.204	6.673	3.537	0.3063	0.2042	0.3063	0.53	0.56	0.204	3.657	0.00250	0.780
1.020	0.204	6.538	3.662	0.3060	0.2550	0.2550	0.56	0.61	0.204	3.850	0.00229	0.778
1.020	0.204	6.497	3.703	0.3060	0.2550	0.2550	0.57	0.60	0.204	3.826	0.00229	0.778
1.020	0.204	6.456	3.744	0.3060	0.2550	0.2550	0.58	0.59	0.204	3.802	0.00230	0.778
1.020	0.204	6.435	3.765	0.3060	0.2550	0.2550	0.59	0.59	0.204	3.789	0.00229	0.778
1.018	0.204	6.423	3.757	0.3054	0.3054	0.2036	0.59	0.66	0.204	4.041	0.00211	0.776
1.018	0.204	6.359	3.821	0.3054	0.3054	0.2036	0.60	0.65	0.204	4.001	0.00211	0.776
1.018	0.204	6.280	3.900	0.3054	0.3054	0.2036	0.62	0.63	0.204	3.952	0.00211	0.776
1.018	0.204	6.222	3.958	0.3054	0.3054	0.2036	0.64	0.62	0.204	3.915	0.00211	0.776
1.016	0.203	6.256	3.904	0.3048	0.3556	0.1524	0.62	0.71	0.203	4.205	0.00194	0.774
1.016	0.203	6.214	3.946	0.3048	0.3556	0.1524	0.64	0.70	0.203	4.177	0.00194	0.774
1.016	0.203	6.102	4.058	0.3048	0.3556	0.1524	0.67	0.68	0.203	4.101	0.00194	0.774
1.016	0.203	6.066	4.094	0.3048	0.3556	0.1524	0.68	0.67	0.203	4.077	0.00194	0.774
1.015	0.203	5.556	4.594	0.3045	0.4060	0.1015	0.83	0.65	0.203	4.010	0.00178	0.772
1.015	0.203	5.442	4.708	0.3045	0.4060	0.1015	0.87	0.63	0.203	3.928	0.00178	0.772
1.015	0.203	5.385	4.765	0.3045	0.4060	0.1015	0.89	0.62	0.203	3.887	0.00178	0.772
1.013	0.203	6.037	4.093	0.3039	0.4559	0.05065	0.68	0.85	0.203	4.652	0.00164	0.770
1.013	0.203	5.789	4.341	0.3039	0.4559	0.05065	0.75	0.79	0.203	4.461	0.00164	0.770
1.013	0.203	5.675	4.455	0.3039	0.4559	0.05065	0.79	0.76	0.203	4.373	0.00164	0.770
1.013	0.203	5.643	4.487	0.3039	0.4559	0.05065	0.80	0.75	0.203	4.349	0.00164	0.770
1.012	0.202	5.619	4.501	0.3036	0.5060	0.00	0.80	0.85	0.202	4.647	0.00151	0.768
1.012	0.202	5.456	4.664	0.3036	0.5060	0.00	0.86	0.80	0.202	4.512	0.00151	0.768

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-5: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 0.5 M based on $\varepsilon(\text{Th}^{4+},\text{Cl}^{-})$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

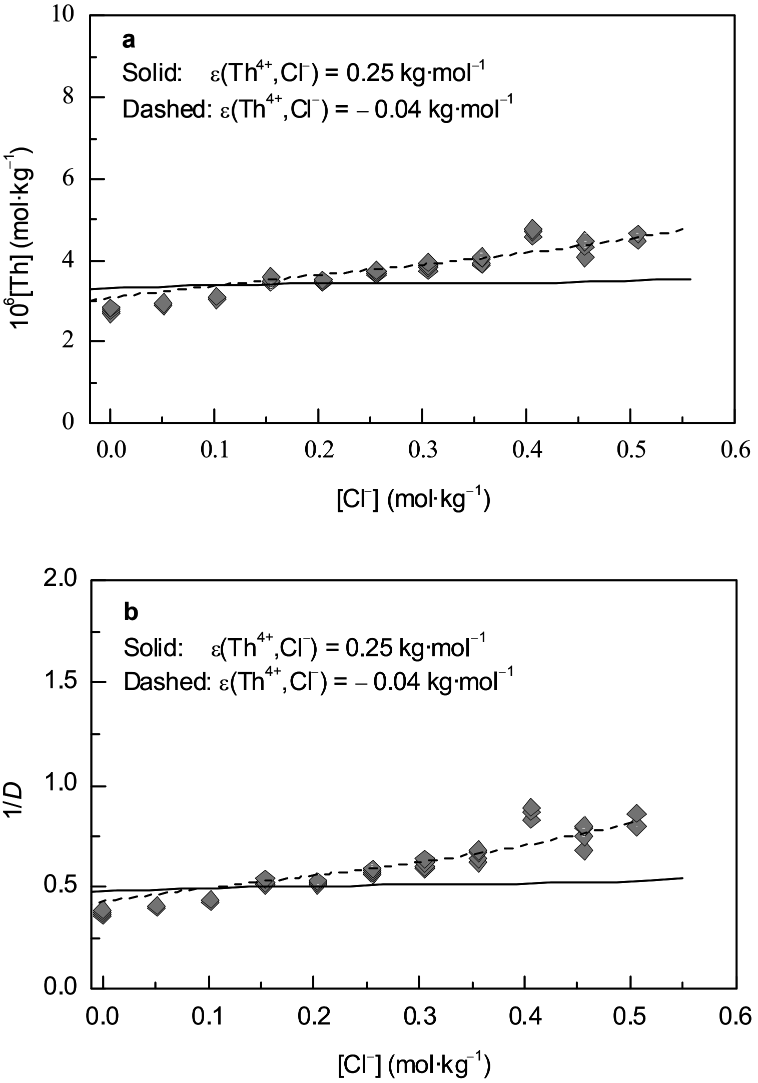


Table A-14: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 0.7 M based on $\varepsilon(\mathrm{Th^{4+}, Cl^-})$ = (0.08 ± 0.10) kg·mol^{-1} and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-6.

Experimental [1952WAG/STO], I_c = 0.7 M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c[a]	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.037	0.207	6.960	3.410	0.5185	0.00	0.7259	0.49	0.60	0.207	3.881	0.00289	0.815
1.037	0.207	6.849	3.521	0.5185	0.00	0.7259	0.51	0.58	0.207	3.819	0.00289	0.815
1.037	0.207	6.756	3.614	0.5185	0.00	0.7259	0.54	0.57	0.207	3.767	0.00290	0.815
1.035	0.207	6.756	3.594	0.5175	0.05175	0.6728	0.53	0.63	0.207	3.981	0.00269	0.813
1.035	0.207	6.656	3.694	0.5175	0.05175	0.6728	0.56	0.61	0.207	3.922	0.00269	0.813
1.035	0.207	6.613	3.737	0.5175	0.05175	0.6728	0.57	0.60	0.207	3.897	0.00269	0.813
1.034	0.207	6.463	3.878	0.517	0.1034	0.6204	0.60	0.64	0.207	4.043	0.00250	0.811
1.034	0.207	6.422	3.918	0.517	0.1034	0.6204	0.61	0.64	0.207	4.018	0.00250	0.811
1.034	0.207	6.363	3.977	0.517	0.1034	0.6204	0.63	0.63	0.207	3.981	0.00250	0.811
1.033	0.207	6.396	3.934	0.5165	0.1550	0.5682	0.62	0.70	0.207	4.248	0.00232	0.809
1.033	0.207	6.112	4.218	0.5165	0.1550	0.5682	0.69	0.65	0.207	4.060	0.00232	0.809
1.033	0.207	6.059	4.271	0.5165	0.1550	0.5682	0.71	0.64	0.207	4.025	0.00232	0.809
1.031	0.206	6.248	4.062	0.5155	0.2062	0.5155	0.65	0.74	0.206	4.383	0.00216	0.807
1.031	0.206	6.211	4.099	0.5155	0.2062	0.5155	0.66	0.73	0.206	4.357	0.00216	0.807
1.031	0.206	6.174	4.136	0.5155	0.2062	0.5155	0.67	0.72	0.206	4.331	0.00215	0.807
1.030	0.206	5.985	4.315	0.515	0.2575	0.4635	0.72	0.76	0.206	4.455	0.00201	0.805
1.030	0.206	5.971	4.329	0.515	0.2575	0.4635	0.73	0.76	0.206	4.445	0.00201	0.805
1.028	0.206	5.824	4.456	0.514	0.3084	0.4112	0.77	0.80	0.206	4.577	0.00186	0.803
1.028	0.206	5.737	4.543	0.514	0.3084	0.4112	0.79	0.78	0.206	4.508	0.00187	0.803
1.028	0.206	5.695	4.585	0.514	0.3084	0.4112	0.81	0.77	0.206	4.475	0.00186	0.803
1.026	0.205	5.691	4.569	0.513	0.3591	0.3591	0.80	0.85	0.205	4.720	0.00173	0.801
1.026	0.205	5.555	4.705	0.513	0.3591	0.3591	0.85	0.81	0.205	4.607	0.00174	0.801
1.025	0.205	5.352	4.898	0.5125	0.4100	0.3075	0.92	0.85	0.205	4.708	0.00161	0.799
1.025	0.205	5.327	4.923	0.5125	0.4100	0.3075	0.92	0.84	0.205	4.686	0.00162	0.799
1.025	0.205	5.284	4.966	0.5125	0.4100	0.3075	0.94	0.83	0.205	4.648	0.00161	0.799
1.023	0.205	5.376	4.854	0.5115	0.4604	0.2558	0.90	0.95	0.205	4.989	0.00150	0.797
1.023	0.205	5.336	4.894	0.5115	0.4604	0.2558	0.92	0.94	0.205	4.952	0.00150	0.797
1.023	0.205	5.323	4.907	0.5115	0.4604	0.2558	0.92	0.93	0.205	4.940	0.00150	0.797
1.023	0.205	5.287	4.943	0.5115	0.4604	0.2558	0.94	0.92	0.205	4.906	0.00150	0.797
1.022	0.204	5.180	5.040	0.511	0.5110	0.2044	0.97	0.99	0.204	5.097	0.00140	0.795
1.022	0.204	5.097	5.123	0.511	0.5110	0.2044	1.01	0.96	0.204	5.015	0.00140	0.795
1.022	0.204	5.059	5.161	0.511	0.5110	0.2044	1.02	0.95	0.204	4.978	0.00140	0.795

[a] Based on estimated conversion factors for mixtures of electrolytes.

Figure A-6: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 0.7 M based on $\varepsilon(\text{Th}^{4+},\text{Cl}^-)$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

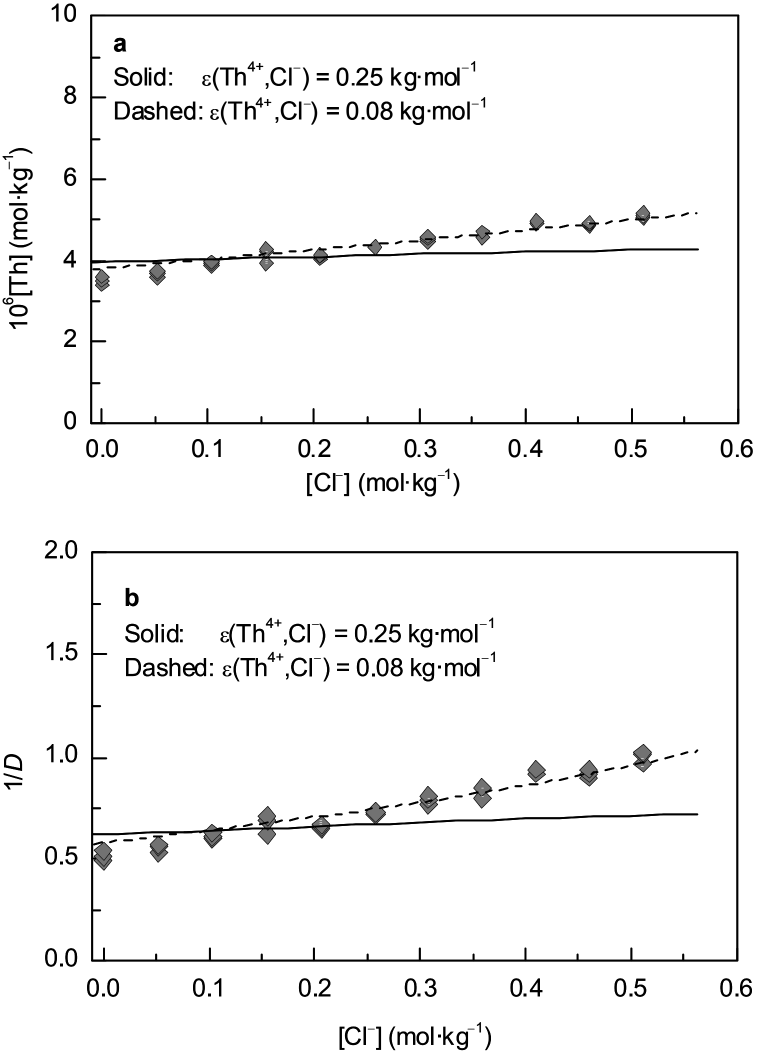


Table A-15: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 1.0 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.13 ± 0.16) $\mathrm{kg\cdot mol^{-1}}$ and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-7.

Experimental [1952WAG/STO], I_c = 1.0 M								Predicted				
Concentrations (m)									Concentrations (m)			
m/c^a	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.051	0.210	6.610	3.900	0.8408	0.00	1.051	0.59	0.68	0.210	4.253	0.00279	0.874
1.048	0.210	6.201	4.279	0.8384	0.1048	0.9432	0.69	0.73	0.210	4.435	0.00243	0.869
1.045	0.209	5.838	4.612	0.836	0.209	0.836	0.79	0.80	0.209	4.638	0.00211	0.864
1.042	0.208	5.725	4.695	0.8336	0.3126	0.7294	0.82	0.94	0.208	5.048	0.00184	0.860
1.039	0.208	5.328	5.062	0.8312	0.4156	0.6234	0.95	1.01	0.208	5.211	0.00160	0.855
1.036	0.207	5.424	4.936	0.8288	0.5180	0.518	0.91	1.31	0.207	5.880	0.00140	0.850
1.034	0.207	4.809	5.531	0.8272	0.6204	0.4136	1.15	1.28	0.207	5.805	0.00122	0.846
1.031	0.206	4.840	5.470	0.8248	0.7217	0.3093	1.13	1.68	0.206	6.466	0.00107	0.841
1.028	0.206	4.356	5.924	0.8224	0.8224	0.2056	1.36	1.67	0.206	6.437	0.00093	0.837
1.025	0.205	3.912	6.338	0.82	0.9225	0.1025	1.62	1.66	0.205	6.390	0.00082	0.833
1.022	0.204	3.488	6.732	0.8176	1.022	0.00	1.93	1.60	0.204	6.293	0.00072	0.828
1.051	0.210	6.565	3.945	0.8408	0.00	1.051	0.60	0.67	0.210	4.224	0.00279	0.874
1.048	0.210	6.023	4.457	0.8384	0.1048	0.9432	0.74	0.70	0.210	4.308	0.00243	0.869
1.045	0.209	5.649	4.801	0.836	0.2090	0.836	0.85	0.75	0.209	4.488	0.00211	0.864
1.042	0.208	5.663	4.757	0.8336	0.3126	0.7294	0.84	0.92	0.208	4.994	0.00184	0.860
1.039	0.208	5.169	5.221	0.8312	0.4156	0.6234	1.01	0.95	0.208	5.056	0.00160	0.855
1.036	0.207	4.933	5.427	0.8288	0.5180	0.518	1.10	1.07	0.207	5.348	0.00140	0.850
1.034	0.207	4.575	5.765	0.8272	0.6204	0.4136	1.26	1.15	0.207	5.522	0.00122	0.846
1.031	0.206	4.314	5.996	0.8248	0.7217	0.3093	1.39	1.27	0.206	5.764	0.00107	0.841
1.028	0.206	4.196	6.084	0.8224	0.8224	0.2056	1.45	1.52	0.206	6.201	0.00093	0.837
1.025	0.205	3.648	6.602	0.82	0.9225	0.1025	1.81	1.39	0.205	5.959	0.00082	0.833
1.022	0.204	3.351	6.869	0.8176	1.022	0.00	2.05	1.45	0.204	6.046	0.00072	0.828

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-7: Observed [1952WAG/STO] and NONLINT-SIT predictions for $I_c = 1.0$ M based on $\varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-)$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

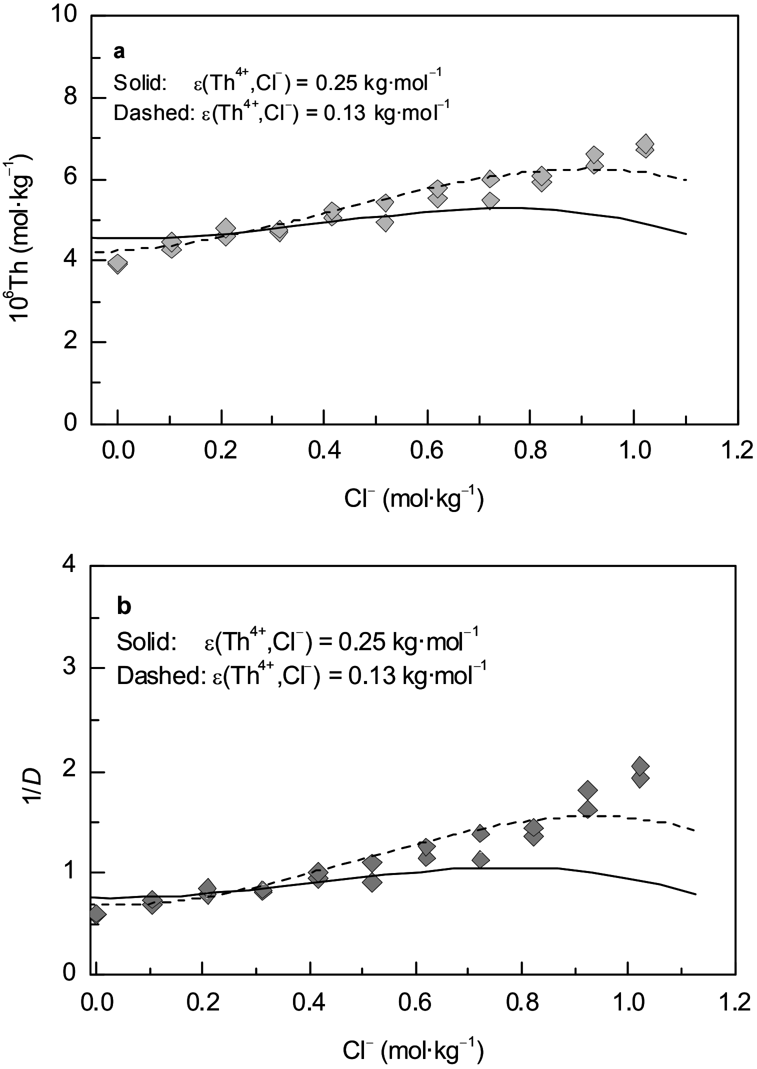


Table A-16: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 2.0 M based on $\varepsilon(Th^{4+}, Cl^-)$ = (0.23 ± 0.12) $kg \cdot mol^{-1}$ and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-8.

Experimental [1952WAG/STO], I_c = 2.0M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c^a	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.106	0.221	5.614	5.446	1.991	0.00	2.212	0.97	1.19	0.221	6.001	0.00629	1.189
1.106	0.221	5.475	5.585	1.991	0.00	2.212	1.02	1.12	0.221	5.852	0.00629	1.189
1.100	0.220	4.933	6.067	1.980	0.2200	1.98	1.23	1.33	0.220	6.277	0.00490	1.173
1.100	0.220	4.846	6.154	1.980	0.2200	1.98	1.27	1.28	0.220	6.166	0.00490	1.173
1.093	0.219	4.425	6.505	1.967	0.4372	1.749	1.47	1.56	0.219	6.657	0.00382	1.157
1.087	0.217	4.041	6.829	1.957	0.6522	1.522	1.69	1.96	0.217	7.203	0.00299	1.142
1.087	0.217	3.924	6.946	1.957	0.6522	1.522	1.77	1.81	0.217	6.995	0.00299	1.142
1.081	0.216	3.568	7.242	1.946	0.8648	1.297	2.03	2.28	0.216	7.517	0.00234	1.127
1.081	0.216	3.454	7.356	1.946	0.8648	1.297	2.13	2.06	0.216	7.277	0.00234	1.127
1.074	0.215	3.159	7.581	1.933	1.074	1.074	2.40	2.66	0.215	7.809	0.00185	1.112
1.068	0.214	2.774	7.906	1.922	1.282	0.8544	2.85	3.09	0.214	8.068	0.00146	1.097
1.062	0.212	2.279	8.341	1.912	1.487	0.6372	3.66	2.74	0.212	7.779	0.00115	1.083
1.056	0.211	2.233	8.327	1.901	1.690	0.4224	3.73	5.45	0.211	8.923	0.00092	1.070
1.056	0.211	2.209	8.351	1.901	1.690	0.4224	3.78	5.09	0.211	8.827	0.00091	1.070
1.049	0.210	1.847	8.643	1.888	1.888	0.2098	4.68	4.46	0.210	8.567	0.00073	1.056
1.049	0.210	1.621	8.869	1.888	1.888	0.2098	5.47	2.53	0.210	7.520	0.00073	1.056
1.043	0.209	1.696	8.734	1.877	2.086	0.00	5.15	7.25	0.209	9.166	0.00058	1.043
1.043	0.209	1.617	8.813	1.877	2.086	0.00	5.45	5.17	0.209	8.740	0.00058	1.043

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-8: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 2.0 M based on $\varepsilon(\text{Th}^{4+},\text{Cl}^-)$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

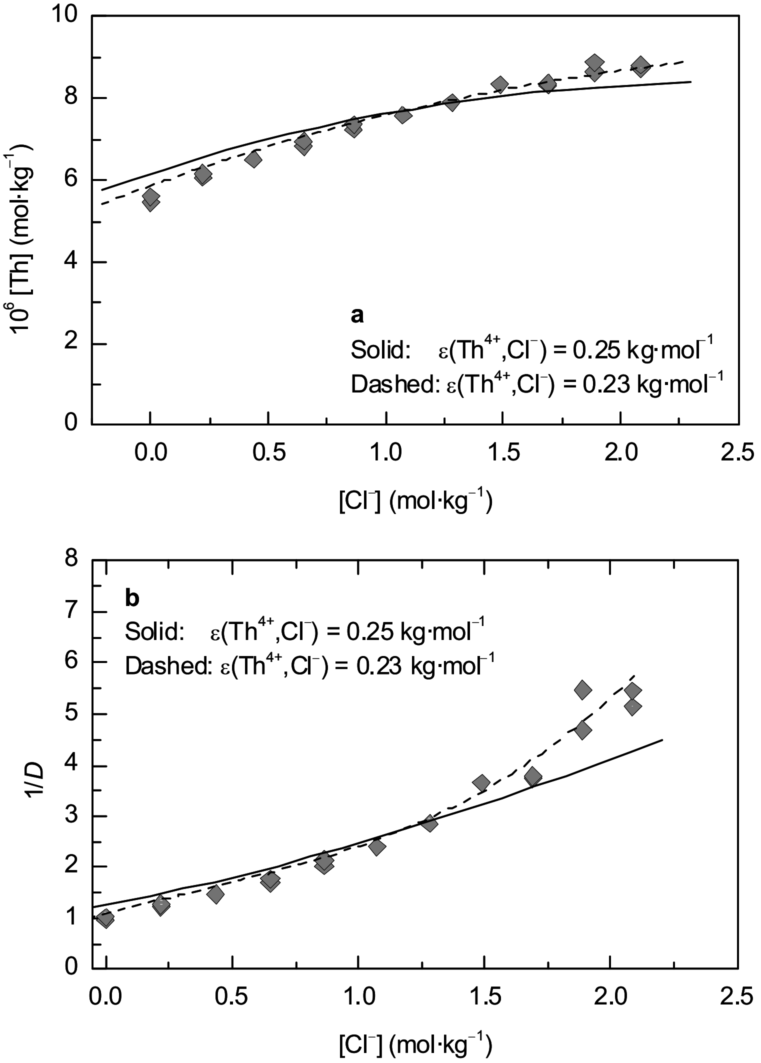


Table A-17: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 4.0 M based on $\varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-)$ = (0.26 ± 0.22) $\mathrm{kg \cdot mol^{-1}}$ and other thermodynamic data listed in Table A-12. Selected data plotted in Figure VIII-8.

Experimental [1952WAG/STO], I_c = 4.0 M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c[a]	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.236	0.396	9.810	2.550	4.548	0.00	4.944	0.26	0.26	0.396	2.570	0.19190	2.698
1.236	0.396	9.581	2.779	4.548	0.00	4.944	0.29	0.25	0.396	2.510	0.19201	2.698
1.218	0.390	8.066	4.114	4.482	0.609	4.263	0.51	0.38	0.390	3.347	0.09361	2.566
1.218	0.390	7.758	4.422	4.482	0.609	4.263	0.57	0.36	0.390	3.219	0.09360	2.566
1.200	0.384	6.818	5.182	4.416	1.200	3.600	0.76	0.58	0.384	4.404	0.04647	2.442
1.200	0.384	6.704	5.296	4.416	1.200	3.600	0.79	0.56	0.384	4.331	0.04639	2.442
1.182	0.378	5.656	6.164	4.35	1.773	2.955	1.09	0.90	0.378	5.597	0.02350	2.326
1.182	0.378	5.629	6.191	4.35	1.773	2.955	1.10	0.89	0.378	5.570	0.02350	2.327
1.164	0.373	4.392	7.248	4.284	2.328	2.328	1.65	1.29	0.373	6.558	0.01211	2.218
1.164	0.373	4.279	7.361	4.284	2.328	2.328	1.72	1.22	0.373	6.389	0.01209	2.218
1.157	0.370	3.883	7.687	4.258	2.545	2.083	1.98	1.43	0.370	6.802	0.00934	2.177
1.157	0.370	3.831	7.739	4.258	2.545	2.083	2.02	1.38	0.370	6.711	0.00934	2.177
1.150	0.368	3.722	7.778	4.232	2.760	1.840	2.09	1.98	0.368	7.643	0.00722	2.137
1.150	0.368	3.674	7.826	4.232	2.760	1.840	2.13	1.91	0.368	7.545	0.00723	2.137
1.143	0.366	3.412	8.018	4.206	2.972	1.600	2.35	2.53	0.366	8.192	0.00561	2.099
1.143	0.366	3.266	8.164	4.206	2.972	1.600	2.50	2.18	0.366	7.841	0.00561	2.099
1.136	0.364	2.943	8.417	4.18	3.181	1.363	2.86	2.63	0.364	8.230	0.00436	2.061
1.136	0.364	2.905	8.455	4.18	3.181	1.363	2.91	2.51	0.364	8.123	0.00437	2.061
1.129	0.361	2.720	8.570	4.155	3.387	1.129	3.15	3.62	0.361	8.845	0.00341	2.024
1.129	0.361	2.675	8.615	4.155	3.387	1.129	3.22	3.36	0.361	8.699	0.00341	2.024
1.122	0.359	2.397	8.823	4.129	3.590	0.8976	3.68	4.13	0.359	9.031	0.00267	1.987
1.122	0.359	2.382	8.838	4.129	3.590	0.8976	3.71	4.00	0.359	8.975	0.00267	1.987
1.114	0.357	2.232	8.908	4.1	3.788	0.6684	3.99	6.64	0.357	9.682	0.00209	1.950
1.114	0.357	2.228	8.912	4.1	3.788	0.6684	4.00	6.55	0.357	9.664	0.00209	1.951
1.107	0.354	1.919	9.151	4.074	3.985	0.4428	4.77	6.49	0.354	9.592	0.00164	1.916
1.107	0.354	1.899	9.171	4.074	3.985	0.4428	4.83	6.02	0.354	9.492	0.00165	1.916
1.100	0.352	1.806	9.194	4.048	4.180	0.2200	5.09	17.03	0.352	10.39	0.00130	1.883
1.100	0.352	1.741	9.259	4.048	4.180	0.2200	5.32	10.22	0.352	10.02	0.00130	1.883
1.093	0.350	1.579	9.351	4.022	4.372	0.00	5.92	20.86	0.350	10.43	0.00103	1.850
1.093	0.350	1.497	9.433	4.022	4.372	0.00	6.30	9.53	0.350	9.892	0.00103	1.850

a: Based on estimated conversion factors for mixtures of electrolytes.

Table A-18: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 6.0 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.25 ± 0.10) kg·mol^{-1} and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-9.

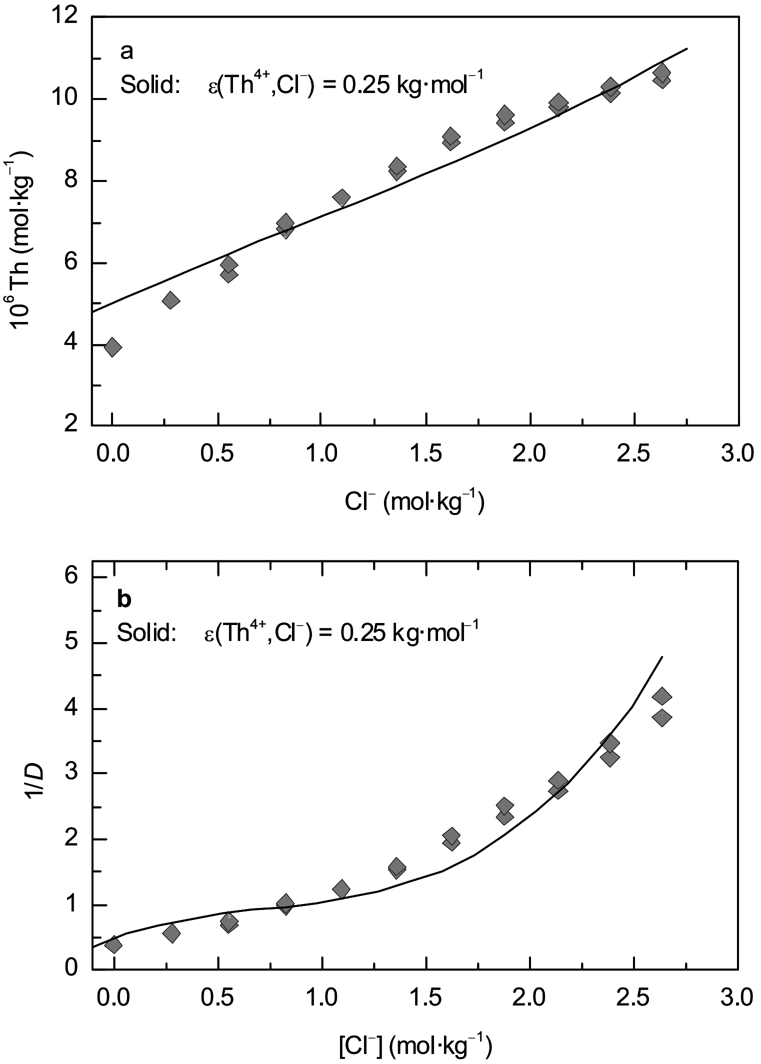
Experimental [1952WAG/STO], I_c = 6.0 M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c[a]	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.405	0.450	10.11	3.942	7.980	0.00	8.430	0.39	0.56	0.450	5.054	30.505	8.020
1.405	0.450	10.11	3.942	7.980	0.00	8.430	0.39	0.56	0.450	5.054	30.505	8.020
1.396	0.447	8.892	5.068	7.929	0.2792	8.097	0.57	0.66	0.447	5.565	21.064	7.784
1.396	0.447	8.892	5.068	7.929	0.2792	8.097	0.57	0.66	0.447	5.565	21.064	7.784
1.388	0.444	8.165	5.715	7.884	0.5552	7.773	0.70	0.85	0.444	6.394	14.731	7.570
1.388	0.444	7.931	5.949	7.884	0.5552	7.773	0.75	0.81	0.444	6.211	14.752	7.570
1.379	0.441	6.965	6.825	7.833	0.8274	7.447	0.98	0.97	0.441	6.786	10.266	7.351
1.379	0.441	6.827	6.963	7.833	0.8274	7.447	1.02	0.93	0.441	6.651	10.259	7.351
1.370	0.438	6.116	7.584	7.782	1.096	7.124	1.24	1.17	0.438	7.390	7.167	7.137
1.362	0.436	5.383	8.237	7.736	1.362	6.810	1.53	1.45	0.436	8.057	5.056	6.944
1.362	0.436	5.259	8.361	7.736	1.362	6.810	1.59	1.37	0.436	7.871	5.058	6.944
1.353	0.433	4.586	8.944	7.685	1.624	6.494	1.95	1.67	0.433	8.469	3.558	6.745
1.353	0.433	4.436	9.094	7.685	1.624	6.494	2.05	1.53	0.433	8.192	3.553	6.745
1.344	0.430	4.012	9.428	7.634	1.882	6.182	2.35	2.10	0.430	9.099	2.512	6.553
1.344	0.430	3.829	9.611	7.634	1.882	6.182	2.51	1.83	0.430	8.684	2.514	6.553
1.336	0.428	3.563	9.797	7.588	2.138	5.878	2.75	2.88	0.428	9.919	1.793	6.379
1.336	0.428	3.426	9.934	7.588	2.138	5.878	2.90	2.50	0.428	9.538	1.793	6.379
1.327	0.425	3.122	10.15	7.537	2.389	5.573	3.25	3.99	0.425	10.61	1.274	6.199
1.327	0.425	2.969	10.30	7.537	2.389	5.573	3.47	3.17	0.425	10.09	1.277	6.199
1.318	0.422	2.712	10.47	7.486	2.636	5.272	3.86	5.69	0.422	11.21	0.911	6.026
1.318	0.422	2.539	10.64	7.486	2.636	5.272	4.19	3.92	0.422	10.50	0.912	6.026

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-9: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 6.0 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.25 ± 0.10) kg·mol^{-1} and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations



The conclusion from these calculations and those summarised under [1950DAY/STO] is that the experimental data can be described well both with the complex formation (as shown in [1952WAG/STO]) and the activity coefficient model. This review has used the complex formation model and the SIT to calculate the equilibrium constant $\log_{10}\beta_1^{\circ}$ = (1.70 ± 0.10) as shown in Figure VIII-9 (Section VIII.2.2.1). This value is in reasonable agreement with the one obtained in [1952WAG/STO] using the Debye-Hückel term only, $\log_{10}\beta_1^{\circ} = 1.38$. The final issue is: How do we describe the experimental data and what method should be used in chemical modelling? The experimental data from [2005HEN/TUT] demonstrate unequivocally that chloride complexes are formed; this fact and the use of the complex formation model in previous volumes in this series is the reason why this review prefers the complex formation model. However, the uncertainty in the equilibrium constants is large and the only chemical conclusion that can be supported is that the thorium(IV) chloride complexes are very weak and therefore of minor importance in systems where ligands that form stronger complexes are present. It should also be emphasised that modelling the Th-Cl systems should either use ion-interaction parameter or ion complexes but not both.

[1953EYR/WES]

The enthalpy of solution of thorium sesquisulphide in 6.000 M HCl media was determined at 298.15 K according to reaction:

$$Th_2S_3(cr) + 8H^+ \text{ (in 6.000 M HCl +)} \rightarrow \{2Th^{4+} + 3H_2S\} \text{ (in 6.000 M HCl)} + H_2(g),$$

leading to the standard enthalpy of formation of this compound.

Preliminary tests indicated that (96.95 ± 0.20)% of the samples dissolved in the medium used, leaving a (3.05 ± 0.20)% residue of a mixture of ThOS and ThO_2. It was also shown by titrimetry that the H_2S produced by the dissolution, corresponded to a compound with a S/Th ratio of (1.500 ± 0.005). Gravimetric analyses for the thorium in the individual calorimetric solutions were also carried out, as well as determinations of the amount of H_2S remaining in each of these solutions (about 94%). Corrections were made by the authors for the partial loss of H_2S to the gas phase and the evolution of hydrogen in the dissolution reaction. These corrections included the saturation of the evolving gases by the components of the HCl solutions

Three dissolution experiments were carried out in 6.000 M HCl and three others in the same medium containing 0.005 M Na_2SiF_6. No detectable heat effect was detected due to the presence of Na_2SiF_6, which, however, appeared to increase the rate of dissolution. As the same authors [1950EYR/WES] had established as −(1.25 ± 0.42) $kJ\cdot mol^{-1}$ the effect of the presence of 0.005 M Na_2SiF_6 in the dissolution of Th(cr) in 6.000 M HCl, we have treated separately the two sets of data for the dissolution of $Th_2S_3(cr)$.

In carrying the correction for the partial evaporation of H_2S we have used the value selected in this review, (18.0 ± 1.6) $kJ\cdot mol^{-1}$ for the process $H_2S(aq) \rightleftharpoons H_2S(g)$

corresponding to the hypothetical standard state of unit molality, as such data are not available in 6.000 M HCl. Eyring and Westrum [1953EYR/WES] had used for this process a value of 19.2 kJ·mol^{-1}; this leads to a minute correction in the enthalpies of solution: $-(556.1 \pm 0.4)$ and $-(555.8 \pm 0.4)$ kJ·mol^{-1}, in the absence and presence of 0.005 M Na_2SiF_6, respectively. The use of $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = $-(758.957 \pm 1.600)$ kJ·mol^{-1} (see Section VI.1) and $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl$-$0.005 M Na_2SiF_6) = $-(760.207 \pm 1.700)$ kJ·mol^{-1} (taking into account the influence of the fluorosilicate ion, $-(1.25 \pm 0.42)$ kJ·mol^{-1}, see Section VIII.2.1.3.1) and of the selected value for $\Delta_f H_m$ (H_2S, aq, 298.15 K) = $-(38.6 \pm 1.5)$ kJ·mol^{-1} leads, for $\Delta_f H_m$ (Th_2S_3, cr, 298.15 K) to the values $-(1077.6 \pm 5.5)$ and $-(1080.4 \pm 5.6)$ kJ·mol^{-1} from the 6.000 M HCl and (6.00 + 0.005 M Na_2SiF_6) media, respectively. In these calculations, small effects due to the dilution of the media by the reacting species were neglected, the thorium concentration in the solutions being in the millimolar range.

[1953GRI/SKO]

The heat capacity of Th(cr) was measured from 18 to 300 K, at 3$-$4 K intervals. A thorium rod, 7.5 cm long × 3.8 cm diameter was used for the measurements. The major impurities in the metal were 0.04% N, 0.06% O and 0.028% Si (mass%). The original experimental data are not given, only smoothed data at 20 to 300 K being tabulated. The authors state that agreement of the experimental data with the smoothed curve was generally well within 0.1%, but deviations of up to 0.2% were observed between 135 and 155 K. The uncertainties in $C_{p,m}$ are estimated by the authors to be 1% at 20 K, decreasing to 0.3% at 30 K and 0.1% above 35 K. For the entropy calculation, $C_{p,m}$ was extrapolated below 20 K using a Debye function with a Debye temperature of 141.6 K, the mean value from 18 to 28 K. The entropy calculated by the authors is S°_{m} (Th, cr, 298.15 K) = 53.39 J·K^{-1}·mol^{-1}; no uncertainty is given.

[1953OSB/WES]

The heat capacity of ThO_2 was determined in an adiabatic calorimeter from 10.2 to 305.4 K. The heat capacity and entropy at 298.15 K were calculated to be (61.76 ± 0.06) and (65.24 ± 0.08) J·K^{-1}·mol^{-1} respectively; when corrected for the modern atomic weight of thorium, these become 61.74 and 65.23 J·K^{-1}·mol^{-1}. The sample of thoria used was ground from electrically-fused material, and was analysed to have a Th content of (87.54$-$87.93) mass% (theoretical 87.88). Chemical analysis showed the total content of lanthanide elements to be < 150 ppm, similar to the total content of other metals, measured spectroscopically. 53 heat capacity measurements were made, extending from 10.2 to 305.4 K. For the entropy calculations, the heat capacity was extrapolated to 0 K using a Debye function. The heat capacity and entropy from this excellent study were adopted by the review.

[1954ALL/YOS]

The reaction of Th(cr) with iodine from 1395 to 1706 K was investigated by passing iodine vapour, entrained in an inert gas, over the metal in a molybdenum tube. The iodine content of the gas stream both before and after reaction was determined by measurement of the optical density at wavelengths in the 4300 − 4800 Å range, and the partial pressure of the metallic iodide (assumed to be $ThI_4(g)$) was determined by difference. The measurements at the highest temperature (1706 K) gave optical densities greater than unity and were rejected, as were those at the lowest temperature (1395 K), because of the very low, and thus uncertain, optical density. The remaining four measurements were assumed to refer to the equilibrium $Th(cr) + 4I(g) \rightleftharpoons ThI_4(g)$, and the enthalpy and entropy of this reaction at the mean temperature are derived. However, the experimental $\Delta_r S_m$ (1515 K), $-628\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ (as calculated by the review) is much more negative than that calculated from the selected thermal functions, $-306\ J{\cdot}K^{-1}{\cdot}mol^{-1}$. This indicates that the reaction was more complex than that assumed (probably involving lower gaseous iodides) and/or that equilibrium was not achieved. These data are not used in the assessment.

[1954EYE/SEL]

This paper reports an extensive study of the Th-Te system. The ThTe, $ThTe_2$, $ThTe_{2.66}$, and ThOTe phases were prepared and identified from X-ray and chemical analyses. ThTe is simple cubic with the CsCl-type structure (unlike ThS and ThSe, which have the NaCl structure) while ThOTe is tetragonal, isostructural with ThOSe and ThOS. The tellurides are all degraded well below 1273 K when heated *in vacuo*. The Th-Te system is not analogous to the Th-S and the Th-Se systems.

[1954FAU]

Faucherre has studied the solution chemistry of a number of ions known to form basic (*i.e.*, containing coordinated oxide and hydroxide in the solid compounds) salts using pH titrations and measuring the free hydrogen ion concentration. A graphical method was used to analyse the experimental data. The reliability of the methods used by Faucherre can be tested by comparison with the data obtained for the hydrolysis of Bi(III), where there are both experimental and structure chemical data available, *cf.* [1976BAE/MES]. Faucherre suggests that the predominant hydrolysis product is $Bi_4O_4^{4+} \equiv Bi_4(OH)_8^{4+}$, as compared to the very well documented $Bi_6(OH)_{12}^{6+}$. This review concludes that the methods used by Faucherre are not satisfactory, hence we do not accept the evidence for the formation of $Th_4(OH)_8^{8+}$ based on his experimental data.

[1954FER/KAT]

The hydrates of $Th(NO_3)_4(cr)$ and ternary system $Th(NO_3)_4(cr)$-H_2O-HNO_3 were investigated at 298.15 K, by the wet residues method. At this temperature, the stable hydrates are the penta- and tetrahydrate. The ternary system is depicted. The invariant point of the pentahydrate-tetrahydrate-aqueous phases is at 17.70 wt% water and 28.67 wt% $Th(NO_3)_4$ and that of the tetrahydrate-$Th(NO_3)_4$-aqueous phases is at 5.10% water and 21.13% $Th(NO_3)_4$. The authors discuss in some detail the various lower and higher hydrates, but conclude that there is no conclusive evidence that any of these are stable at 298.15 K. The anhydrous solid isolated from the low-water region of the ternary system, of composition suggested by the extrapolation of the 'wet-residues' tie-lines, $Th(NO_3)_4{\cdot}2HNO_3$, showed the same XRD pattern as the addition product of $Th(NO_3)_4$ and nitrogen dioxide, isolated previously.

[1954GAY/LEI]

Gayer and Leider [1954GAY/LEI] studied the solubility of Th(IV) hydroxide in $HClO_4$ and NaOH solutions at 25°C. The solid, designated as thorium hydroxide $ThO(OH)_2(s)$, was precipitated from thorium perchlorate solution by adding an excess of NaOH, washed with water and used for solubility experiments in following media:

(1): 0.020 – 0.811 m $HClO_4$

(2): Dilute $HClO_4$ (pH = 3.12 - 3.44)

(3): 0.010 – 0.865 m NaOH (prepared and stored under N_2 atmosphere)

After shaking the samples 5 – 7 days for equilibration, the Th concentrations were determined colorimetrically. After allowing the solid to settle 3 – 5 days, aliquots were taken from the clear supernatant without filtration or centrifugation to remove polymeric or colloidal species.

- *Solubility in acidic solutions*

For series (1) only the initial $HClO_4$ concentrations are reported, but not the equilibrium pH or $-\log_{10}[H^+]$ values. These data are not useful, because the measured Th concentrations are only 2 – 3 times lower than the initial H^+ concentrations (*e.g.*, [Th] = 0.04 $mol{\cdot}kg^{-1}$ in initially 0.1 m $HClO_4$); since H^+ is consumed by the dissolution of thorium hydroxide, there is no information on the equilibrium H^+ concentration.

In series (2), pH is measured with a glass electrode which is roughly calibrated against two buffer solutions at pH 4 and pH 7. The equilibrium thorium concentrations were found to decrease from $\log_{10}[Th] = -1.42$ at pH 3.12 to $\log_{10}[Th] = -2.00$ at pH 3.4. The equilibrium constants calculated by Gayer and Leider [1954GAY/LEI] for the reactions:

$$ThO(OH)_2(s) + H^+ \rightleftharpoons ThO(OH)^+ + H_2O(l) \quad (A.30)$$

$$ThO(OH)_2(s) + 2H^+ \rightleftharpoons ThO^{2+} + 2H_2O(l) \quad (A.31)$$

$$ThO(OH)_2(s) \rightleftharpoons ThO^{2+} + 2OH^- \quad (A.32)$$

are $\log_{10} {}^*K^\circ_{s,1}$ (A.30) = 1.51, $\log_{10} {}^*K^\circ_{s,2}$ (A.31) = 4.74 and $\log_{10} K^\circ_{s,2}$ (A.32)= – 23.26, respectively. They are based on the assumptions $\gamma_{ThO(OH)^+} = \gamma_{H^+}$ and $\gamma_{ThO^{2+}} = (\gamma_{H^+})^2$;

where γ_{H^+} is calculated with the Debye-Hückel equation. These equilibrium constants are not accepted by this review. It is known from potentiometric studies that $\mathrm{ThO(OH)^+}$ and $\mathrm{ThO^{2+}}$ (equivalent to $\mathrm{Th(OH)_3^+}$ and $\mathrm{Th(OH)_2^{2+}}$) are not the predominant Th(IV) hydroxide complexes at the $\mathrm{H^+}$ and Th concentrations of the solubility studies (1) and (2). Since ionic strength is not kept constant and the pH values, which are not very accurate, vary only in a narrow range, these results are not re-evaluated in the present review. However, it should be noted that the solubility data of [1954GAY/LEI] at pH 3.1 − 3.4 are consistent with solubility data for $\mathrm{ThO_2}$(am, hyd) in numerous studies over more extended pH ranges at I = 0.1, 0.5 or 0.6 M [1964NAB/KUD], [1978RYA/RAI], [1989MOO], [1991FEL/RAI], [2000RAI/MOO], [2002NEC/MUL].

- Solubility in alkaline solutions

From a linear plot of the equilibrium thorium concentrations in NaOH solutions above 0.38 molal (Figure 1 in [1954GAY/LEI]), Gayer and Leider postulated the formation of anionic hydroxide complexes according to the reactions.

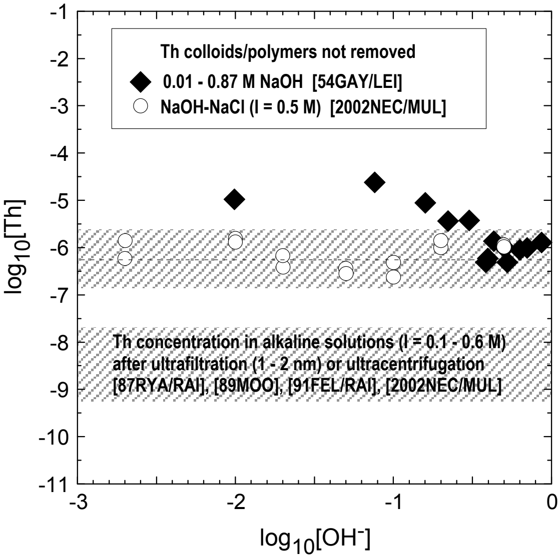
$$\mathrm{ThO(OH)_2(s) + OH^- \rightleftharpoons HThO_3^- + H_2O(l)}\ \text{(equal to } \mathrm{Th(OH)_5^-}\text{)} \qquad \text{(A.33)}$$

$$\mathrm{ThO(OH)_2(s) + 2OH^- \rightleftharpoons ThO_3^{2-} + 2H_2O(l)}\ \text{(equal to } \mathrm{Th(OH)_6^{2-}}\text{)} \qquad \text{(A.34)}$$

The equilibrium constants, calculated assuming $\gamma_{\mathrm{HThO_3^-}} = \gamma_{\mathrm{OH^-}}$ and $\gamma_{\mathrm{ThO_3^{2-}}} = (\gamma_{\mathrm{OH^-}}\ \gamma_{\mathrm{NaOH}})^2$, are $\log_{10} K^{\circ}_{s,5}$(A.33) = $\log_{10} K^{\circ}_{s,6}$(A.34) = −5.80. These values are not accepted by the present review.

As demonstrated in a number of later solubility studies with thorium hydroxide or $\mathrm{ThO_2}$(am, hyd) at constant ionic strength (I = 0.1, 0.5 or 0.6 M) [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002NEC/MUL], there is no evidence for the formation of anionic Th(IV) hydroxide complexes at high pH which would cause an increase of the solubility; in these studies the solubility was found to be constant at a level of $\log_{10}$[Th] = −(8.5 ± 0.8) from pH 6 up to pH 13.5. Figure A-10 demonstrates that Gayer and Leider's solubility data in NaOH solutions, shown in a logarithmic plot of $\log_{10}$[Th] *vs.* $\log_{10}[\mathrm{OH^-}]$, provide no indication for the formation of anionic Th(IV) hydroxide complexes. There is only a scatter due to the fact that, as mentioned above, Gayer and Leider [1954GAY/LEI] have taken the aliquots for Th concentration measurements without filtration or centrifugation to remove polymeric or colloidal species. Their equilibrium thorium concentrations are considerably higher than those measured by other authors after ultracentrifugation or ultrafiltration [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002NEC/MUL]. The data in NaOH solutions above 0.3 molal are comparable with those measured by Neck *et al.* [2002NEC/MUL] in the clear supernatant of the samples, *i.e.*, as done in [1954GAY/LEI] without removal of colloids. The equilibrium thorium concentrations coming from neutral Th(IV) polymers or small colloids in neutral and alkaline solution, also at higher ionic strength, have been discussed in [2004ALT/NEC] and found to be constant at a level of $\log_{10}$[Th] = −(6.3 ± 0.6), independent of ionic strength and pH in the range pH = 6 − 14.

Figure A-10: Solubility data determined by Gayer and Leider [1954GAY/LEI] and Neck *et al.* [2002NEC/MUL] with ThO_2(am, hyd) in NaOH and NaOH-NaCl solutions without removal of polymeric/colloidal Th(IV) species. Thorium concentrations measured in comparable solubility studies after ultrafiltration (1−2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI] or ultracentrifugation [2002NEC/MUL] are indicated for comparison by the lower hatched area.



[1954HIE]

This study of the hydrolysis of Th(IV) has been made at 25°C, using potentiometric technique in a 1M (Na)ClO_4 ionic medium. Full experimental details, including all experimental data are reported. Test solutions with six different total concentration of thorium, Th_{tot} = 1, 2, 5, 10 and 20 mM were investigated over the $-\log_{10}[H^+]$ range 2.0 to 4.0. The experiments were made as titrations by adding known volumes of a standardised NaOH solution; the authors point out that the small amounts of carbonate present in these were not important for the interpretation as it is removed as CO_2 by bubbling nitrogen gas through the test solutions. The acid excess in the Th stock-solution was determined by potentiometric titration giving high confidence in the accuracy of the analytical total concentration of H^+, H_{tot}. The experiments were continued until a precipitate was formed as indicated by drifting emf-values. In order to establish if true equilibrium had been obtained some titrations were also made in the reverse direction (increasing $[H^+]$). The emf potentials began to drift around

$-\log_{10}[\mathrm{H}^+] = 3.0$ and the test solutions were distinctly opaque at $-\log_{10}[\mathrm{H}^+] = 4.7$ at $[\mathrm{Th}]_{\mathrm{tot}} = 2$ mM. The emf values were corrected for the hydrogen ion dependent diffusion potentials.

The values of $\bar{n}_{\mathrm{OH}}$ ranges from approx 0 to 2.7 and all data were used in the graphical analysis. From the plots of $\bar{n}_{\mathrm{OH}}$ *vs.* $-\log_{10}[\mathrm{H}^+]$ the author suggested that the complexes formed were of the "core-and-link" type, $\mathrm{Th}\{(\mathrm{OH})_3\mathrm{Th}\}_n^{(4+n)+}$, where Th is the core and "$(\mathrm{OH})_3\mathrm{Th}$" the link. This model implies an unlimited series of complexes that can be described using a two-parameter approximation:

$$(n{+}1)\mathrm{Th}^{4+} + 3n\mathrm{H_2O} \rightleftharpoons \mathrm{Th}\{(\mathrm{OH})_3\mathrm{Th}\}_n^{(4+n)+} + 3n\mathrm{H}^+ \qquad k_n$$

The ratio k_{n+1}/k_n is the equilibrium constant for the addition of a new link:

$$\mathrm{Th}\{(\mathrm{OH})_3\mathrm{Th}\}_n^{(4+n)+} + \mathrm{Th}^{4+} + 3\mathrm{H_2O} \rightleftharpoons \mathrm{Th}\{(\mathrm{OH})_3\mathrm{Th}\}_{n+1}^{(5+n)+} + 3\mathrm{H}^+$$

In this two-parameter approximation three different models were tested, $k_n = k_0k^n$, $k_n = k_0nk^n$ and $k_n = k_0k^n/n$. Hietanen found that the experimental data could be described equally well by these models with k_0 between 0.5 to 1.0 for the first two models and about 0.1 for the third. The value of $\log_{10} k$ for the three models were − 7.50, − 7.65 and −9.15, respectively. The "core-and-link" model is related to chain structures found in solid state for so called "basic salts", thorium hydroxide sulphate and thorium hydroxide chromate ([1949SIL/LUN], [1950LUN]). However, in solution systems, a model with a very large number of complexes does not make chemical sense and the model was also abandoned in later studies.

The experimental data indicate quite clearly that polynuclear complexes are formed and that only small amounts of mononuclear complexes are present in the system under the experimental conditions used. The experimental data were reanalysed using least-squares methods as discussed in [1964HIE/SIL].

[1954HOC/JOH]

The vapour pressure over $\mathrm{ThO_2}$(cr) (no analysis given) in a tantalum cell was determined by Knudsen effusion from 2398 to 2676 K, and with admixed W(cr) from 2389 to 2661 K; the pressures were the same in the two cases. The authors note that some decomposition to ThO(g) did occur at the highest temperatures. However, it is now known that under these conditions, the oxygen potential is so low that the major species in the vapour is ThO(g) rather than $\mathrm{ThO_2}$(g) over the whole temperature range, and these results are discussed under ThO(g) in Section VII.1.1.

The authors suggested that the material formed from $\mathrm{ThO_2}$ and Th at 2150 K, which had an fcc cell parameter of 4.31 Å was ThO(cr). However, this lattice constant is much smaller than the cell sizes of the firmly established U(C,N,O) and Pu(C,N,O) phases, and could not have been ThO(cr), pure or impure.

[1954KRA/HOL]

The hydrolysis of Th(IV) was studied at 25°C in 1 M (Na)ClO_4; the experimental data cover the Th_{tot} concentration range from 2.5×10^{-4} to 1.5×10^{-2} M and the $-\log_{10}[H^+]$ range from 2.3 to 3.7. The values of $\bar{n}_{OH}$ vary from 0.03 to about 2.5. The investigators checked the reversibility of the titration data, if precipitation occurred and also arranged the experiment in such a way that the variation in the activity factors was minimised. They also noted that equilibrium was rapidly attained and that the solutions remained clear at $\bar{n}_{OH} < 2$. Experimental data are reported, but the number of reported experimental points is much smaller than in the study by Hietanen [1954HIE]; more data are given in Figure 3 of [1965BAE/MEY]. The analysis of the data has been made using approximations and graphical methods and the reported equilibrium constants therefore do not have the highest accuracy. The reported values are: $\log_{10}{}^*\beta_{1,1} = -4.3$, $\log_{10}{}^*\beta_{2,1} = -7.8$ and $\log_{10}{}^*\beta_{2,2} = -4.8$.

The authors mention ultracentifugation experiments that indicate the formation of tetranuclear species at $\bar{n}_{OH}$ slightly less than 2 and the formation of aggregates with a much higher nuclearity at $\bar{n}_{OH} > 2$. The primary experimental data $\bar{n}_{OH}(-\log_{10}[H^+])$ in this study agree well with those in [1954HIE]. The chemical model and the deduced equilibrium constants were also checked using the Oak Ridge least squares program by Rush as described in the comments to [1965BAE/MEY].

[1954LOH/OSB]

ThF_4(cr) was prepared from a pure sample of electrically fused ThO_2(cr) by hydrofluorination at 1023 K for 132 h, until a constant weight was attained. Analyses for thorium and fluorine were in excellent agreement with the theoretical values. The heat capacities of a 91 g sample were measured from 5.5 to 298.2 K and are given in a table and a graph. At 298.15 K, $C^{\circ}_{p,m}$(ThF_4, cr) = (110.71 ± 0.13) J·K^{-1}·mol^{-1} and S°_{m}(ThF_4, cr) = (142.06 ± 0.17) J·K^{-1}·mol^{-1}.

[1955PAN/HSE]

The hydrolysis of Th(IV) has been studied at 25°C and different constant concentrations of sodium perchlorate (0.05, 0.1, 0.3 and 0.5 M) by diluting 10.0 mM test solutions of Th(IV) with the ionic medium. The experimental quantities are the pH change and the change in Th(IV) concentration. The glass electrode used was calibrated against pH buffer solutions but the conversion of H^+ activities to H^+ concentrations is not reported in [1955PAN/HSE].

The experimental data were interpreted using two mononuclear complexes, $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$. The reported equilibrium constants are given in Table A-19. The authors have not taken the presence of polynuclear complexes into account and they are predominant in the 10 mM test solution in the pH range studied (approx. 2.7−4.1). For these reasons the equilibrium constants are not accepted by the present review.

Table A-19: Equilibrium constants reported in [1955PAN/HSE]

Ionic strength (M)	$\log_{10}{}^*\beta_1$	$\log_{10}{}^*\beta_2$
0.5	– 4.26	– 8.28
0.3	– 4.12	– 8.19
0.1	– 4.00	– 8.14
0.05	– 3.92	– 8.11
0 [a]	– 3.89 [a]	– 8.09 [a]
Pure water	– 3.77	– 8.09

a The equilibrium constants at zero ionic strength given in [1955PAN/HSE] were derived by extrapolating $\log_{10}{}^*\beta_n$ plotted against $I^{1/2}$ to $I = 0$.

[1955ROB/JEN]

These authors used reaction calorimetry to measure the enthalpies of formation of a number of silicides of Ti, Zr, V, Ta, Mo, W, and Th. For the disilicides, the authors compared the enthalpies of formation and the character of the metal bonding.

Metals and silicon in powdered form were used as starting materials. The major impurities in Si were Al (0.1%), B (< 0.01%), and Fe (< 0.01%), while the thorium sample was reported as containing 98.7% Th, 0.15% Fe, a trace of Si, and the balance thorium oxide. For calorimetry the mixtures of powders in the appropriate stoichiometric ratio were compacted at 20 tons per square inch (2.75 kbar) so as to obtain cylinders 10 mm in diameter and 20 mm high.

The calorimeter (operating at (296 ± 1) K) was calibrated using the aluminothermic reaction $Cr_2O_3 + 2Al \rightleftharpoons Al_2O_3 + 2Cr$ for which a enthalpy change value of – 539.7 kJ·mol^{-1} was reported (a 10% excess Al was assumed not to take part to the reaction), which compares to a literature value of –536.0 kJ·mol^{-1} [1982WAG/EVA]. A mixture of the same composition was used to initiate the reaction to form the silicides.

For $\Delta_f H^\circ_m$ ($ThSi_2$, cr), three determinations were reported, yielding –177.8, – 178.2, and –166.9 kJ·mol^{-1}. X-ray examination showed that the reacted product was “mainly a $ThSi_2$ phase and some ThO_2”, the latter being already present in the starting metal powder. These results, assumed to be valid for 298.15 K, are included in the discussion of the basis for the selection of the enthalpy of formation of $ThSi_2$(cr) (Section XI.2.1).

[1956CHU/STE]

This paper reports the solubilities of the thorium and uranyl phosphates; only the Th(IV) studies will be discussed here. The authors have measured the solubility of two different Th(IV) phosphate solids, $Th_3(PO_4)_4$(s) and $Th(HPO_4)_2$(s) as a function of pH in nitric and sulphuric acid solutions. The solid phases used have been analysed using elemental analysis prior to the solubility experiments, but there is no X-ray data, or information on the composition of the solids after equilibration. The experiments have been made at 19−20°C without an additional ionic medium; the time for equilibration was investigated. The experimental data for $Th_3(PO_4)_4(s)$ were collected at three different pH values, 1.80−2.45, sufficiently low to reduce the importance of hydrolysis. The Th(IV) concentration at equilibrium was measured either using a colorimetric method or by using a Th tracer; the two methods give essentially the same result, but we will discuss only those obtained by the first method. The solubility of Th varies between 3.5 and 0.70 mM in the nitrate solutions but is significantly larger in sulphuric acid, 4.5−1.5 mM, presumably as a result of the formation of sulphate complexes. However the authors have not analysed this. The reported solubility product refers to the reaction:

$$Th_3(PO_4)_4(s) \rightleftharpoons 3Th^{4+} + 4PO_4^{3-}$$

and this value has been calculated from the experimental solubility and total concentration of phosphate at equilibrium using the protonation constants in the H^+- PO_4^{3-} system that differs significantly from the values selected in this review. The authors report $\log_{10} K_s = -(78.0 \pm 1.0)$ in H_2SO_4 solutions and $\log_{10} K_s = -(79.2 \pm 0.8)$ in HNO_3 solutions; these values have not been accepted by the present review, because of poor characterisation of the solid phase in the equilibrium solutions, the lack of information on activity coefficients, doubtful values of the protonation constants of phosphate, too few experimental data and neglect of the formation of Th(IV) complexes with OH^-. The proposed equilibrium constant is much larger than the value proposed in [1994BAG/FOU], $\log_{10} K^{\circ}_{s,0} = -(112 \pm 2.1)$.

The solubility of $Th(HPO_4)_2(s)$ was also studied in nitric and sulphuric acid, but only at two different pH values for each acid. The calculated equilibrium constant for the reaction:

$$Th(HPO_4)_2(s) \rightleftharpoons Th^{4+} + 2HPO_4^{2-}$$

is $\log_{10} K_s = -(26.6 \pm 0.2)$ in nitric acid and $\log_{10} K_s = -(20.9 \pm 0.4)$ in sulphuric acid. When the experiments were repeated using a tracer marked solid, the value $\log_{10} K_s = -19.9$ was obtained, but it is not clear from the paper if these experiments were made in nitric or sulphuric acid. For the same reasons as stated above the proposed solubility product for $Th(HPO_4)_2(s)$ is not accepted by this review. Moskvin *et al.* [1967MOS/ESS] also determined the solubility product for $Th(HPO_4)_2(s)$, where they have taken the formation of phosphate complexes into account; their reported solubility product is $\log_{10} K_s = -26.89$.

[1956FER/KAT]

These authors report the measurement of the enthalpy of solution of $Th(NO_3)_4 \cdot 4H_2O(cr)$ and $Th(NO_3)_4 \cdot 5H_2O(cr)$ in water and in number of organic solvents. They observed, as expected, that the relative enthalpies of solution approximately parallel the base strength of the solvents. The authors also reported the enthalpy of solution of $Th(NO_3)_4$(cr). Analytical results were briefly mentioned for the two hydrates, and an earlier reference [1955FER/KAT] was given for details on the anhydrous salt.

The calorimetric apparatus and procedure were described. Performances were verified using the enthalpy of solution of Na_2CO_3(cr) in 200 H_2O. Calorimetric results at 298.15 K were reported based on two or three determinations. The enthalpy of solution of the anhydrous salt in 2500 H_2O was given as -145.2 kJ·mol^{-1}. This review estimates the uncertainty of this value to be ± 2.0 kJ·mol^{-1}. The tetra- and pentahydrates were dissolved in 350 H_2O and the corresponding enthalpies of solution were reported as $-(32.01)$ kJ·mol^{-1} and -14.85 kJ·mol^{-1}, respectively. Based on the discussion by the authors, this review estimates the uncertainty on these values to ± 1.70 kJ·mol^{-1}.

Using the value adopted in this review for the equilibrium constants (Table VII-17) $\log_{10} {}^*\beta^\circ_{n,m}$ ($\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K), the value $\log_{10} {}^*\beta^\circ_1$ ($\mathrm{Th(NO_3)^{3+}}$, 298.15 K) = (1.3 ± 0.2) and $\log_{10} {}^*\beta^\circ_2$ ($\mathrm{Th(NO_3)_2^{2+}}$, 298.15 K) = (2.3 ± 0.4) (as selected in Section X.1.3.3), calculations of the speciation (assuming ideal aqueous solution) indicate that the dissolution reactions can be approximately represented by:

$$\begin{aligned}\mathrm{Th(NO_3)_4(cr)} + 2500\,\mathrm{H_2O(l)} \rightleftharpoons{}& 0.2387\,\mathrm{Th^{4+}} + 0.3370\,\mathrm{Th(NO_3)^{3+}} +\\ & 0.2384\,\mathrm{Th(NO_3)_2^{2+}} + 0.1730\,\mathrm{Th(OH)^{3+}} +\\ & 0.0079\,\mathrm{Th(OH)_2^{2+}} + 0.0024\,\mathrm{Th_2(OH)_3^{5+}} +\\ & 3.1861\,\mathrm{NO_3^-} + 0.1962\,\mathrm{H^+} \quad \text{in } 2499.8040\ \mathrm{H_2O(l)}\end{aligned}$$

$$\begin{aligned}\mathrm{Th(NO_3)_4{\cdot}4H_2O(cr)} + 350\,\mathrm{H_2O(l)} \rightleftharpoons{}& 0.0284\,\mathrm{Th^{4+}} + 0.2050\,\mathrm{Th(NO_3)^{3+}} +\\ & 0.7426\,\mathrm{Th(NO_3)_2^{2+}} + 0.0223\,\mathrm{Th(OH)^{3+}} +\\ & 0.0011\,\mathrm{Th(OH)_2^{2+}} + 0.0003\,\mathrm{Th_2(OH)_3^{5+}} +\\ & 2.3098\,\mathrm{NO_3^-} + 0.0254\,\mathrm{H^+} \quad \text{in } 353.9746\ \mathrm{H_2O(l)}\end{aligned}$$

$$\begin{aligned}\mathrm{Th(NO_3)_4{\cdot}5H_2O(cr)} + 350\,\mathrm{H_2O(l)} \rightleftharpoons{}& 0.0285\,\mathrm{Th^{4+}} + 0.2053\,\mathrm{Th(NO_3)^{3+}} +\\ & 0.7421\,\mathrm{Th(NO_3)_2^{2+}} + 0.0224\,\mathrm{Th(OH)^{3+}} +\\ & 0.0011\,\mathrm{Th(OH)_2^{2+}} + 0.0003\,\mathrm{Th_2(OH)_3^{5+}} +\\ & 2.3105\,\mathrm{NO_3^-} + 0.0255\,\mathrm{H^+} \quad \text{in } 354.974\ \mathrm{H_2O(l)},\end{aligned}$$

neglecting very minor amounts of the higher hydrolysis species.

As can be seen, the nitrate complexes are, in the main, the dominant thorium species in solution. As there are no experimental values for the enthalpy of formation of these complexes (for either thorium or uranium), only the difference between the enthalpies of solution of the pentahydrate and the tetrahydrate has been used (see Section X.1.3.2) in conjunction with other results, to evaluate $\Delta_f H^\circ_m$ ($Th(NO_3)_4{\cdot}4H_2O$, cr, 298.15 K).

[1956FOM/MAI]

Tributyl phosphate (TBP) forms uncharged complexes with tetravalent actinides in organic solvents in equilibrium with nitric acid solution, a fact that is used in reprocessing of spent nuclear fuel in the Purex process. The chemistry is complicated by the simultaneous extraction of both HNO_3-TBP and An(IV)-TBP complexes. Fomin and Maiorova present a detailed experimental investigation of the complex formation in the Th(IV)-nitrate system using the distribution of Th(IV) between an aqueous $H(NO_3, ClO_4)$ phase and an organic phase containing 1 M TBP in benzene. The experiments have been made at a temperature of (20 ± 2)°C and a constant ionic strength of 2.00 M $H(NO_3, ClO_4)$. This is a careful experimental study where the authors provide all the important experimental details. For the extraction from pure nitrate solution they have quantified the co-extraction of HNO_3 and also determined the composition of the extracted uncharged complex in the organic phase, $Th(NO_3)_4(TBP)_2$(org), and the equilibrium constant for the distribution equilibrium:

$$Th^{4+} + 4NO_3^- + 2TBP(org) \rightleftharpoons Th(NO_3)_4(TBP)_2(org) \qquad K = (36 \pm 2)\ M^{-6}.$$

However, the co-extraction of the complexes $HClO_4(TBP)_p$ and $Th(ClO_4)_4(TBP)_n$(org) was not taken into account by the authors. From the variation of the distribution coefficient of Th(IV) between the aqueous and the organic phase they then deduced the equilibrium constants for the reactions:

$$Th^{4+} + nNO_3^- \rightleftharpoons Th(NO_3)_n^{4-n} \qquad n = 1-4.$$

The nitrate concentration in the aqueous phase varied between 0.226 and 1.717 M and a total of five test solutions were investigated. Even if the measurements and data analysis in [1956FOM/MAI] are made with careful attention to details, this is not sufficient to determine precise values of the four equilibrium constants using a total of five different nitrate concentrations. Fomin and Maiorova propose for the reactions:

$$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+} \qquad \beta_1 = (6.0 \pm 0.5)\ M^{-1}$$

$$Th^{4+} + 2NO_3^- \rightleftharpoons Th(NO_3)_2^{2+} \qquad \beta_2 = (13 \pm 1)\ M^{-2}$$

$$Th^{4+} + 3NO_3^- \rightleftharpoons Th(NO_3^-)_3^+ \qquad \beta_3 = (10 \pm 0.5)\ M^{-3}$$

$$Th^{4+} + 4NO_3^- \rightleftharpoons Th(NO_3)_4(aq) \qquad \beta_4 = (5.5 \pm 0.5)\ M^{-4}.$$

These equilibrium constants have been calculated assuming the activity coefficients for reactants and products to be constant. However, this is not the case when the composition of the aqueous phase is varied as in the system studied by [1956FOM/MAI]. Accordingly it is not possible to distinguish between the formation of weak complexes and activity variations. Moreover, the assumption of constant activity coefficients is incorrect for the thorium complex in the organic phase because the composition of the organic thorium complex in the TBP-benzene phase varies when $HClO_4$ is successively replaced by HNO_3. The complexes $Th(ClO_4)_4(TBP)_n$(org) and $Th(NO_3)_4(TBP)_2$(org) are in equilibrium with pure perchlorate or nitrate aqueous phases, respectively; mixed complexes are probably formed when thorium is extracted from $HClO_4$-HNO_3 mixtures. This effect was not taken into account by

[1956FOM/MAI]. The equilibrium constants proposed for the thorium nitrate complexes are therefore considerably overestimated and not accepted by this review.

[1957LAN/MIE]

The observed exothermic enthalpies of dilution of dilute aqueous solutions of $AlCl_3$, $Th(NO_3)_4$, and $UO_2(NO_3)_2$ are attributed to the hydrolysis of the salts. Addition of the appropriate acid represses the hydrolysis and leads to endothermic enthalpies of dilution. No quantitative thermodynamic information can be derived from this paper.

[1958BEA/MCT]

These authors studied the reactions of the chalcogenides of Ti, Zr, Hf and Th with a series of inorganic and organic reagents. They also gave a number of heats of formation based on combustion calorimetry.

Among results, given without any experimental details, values for the standard enthalpies of formation of Th_2S_3(cr), Th_2Se_3(cr), and Th_2Te_3(cr) were listed as −996, − 937, and −628 $kJ\cdot mol^{-1}$, respectively. As recognised by the authors themselves, the difficulties in obtaining complete and unambiguous reactions with such systems are considerable. In the case of sulphides, the formation of SO_3, or of sulphuric acid, if any moisture is present, can lead to large errors. In the case of the heavier chalcogenides, sublimation of the chalcogen is also possible.

These results are mentioned in this review for information only.

[1958DAR/KEN]

The vapour pressures of ThF_4(cr) and ThF_4(l) were determined, by effusion for the solid (1055 to 1297 K) and the boiling point method for the liquid (1437 to 1595 K). Mass-spectrometric studies showed that the monomer is the only important species in the vapour.

The sample of ThF_4 used was well characterised by X-ray and chemical analysis for thorium; volatile impurities were negligible. The melting point was found to be (1383 ± 2) K, in agreement with an earlier value.

The vapour pressure of the solid was determined by mass-loss effusion from a nickel cell, from 1055 to 1297 K. Corrosion tests showed negligible reaction between Ni and ThF_4, even in the molten state. In one run, the effusate was collected on a tantalum cylinder and was found to be ThF_4, by chemical and X-ray analysis.

The boiling point method was used for the measurements on the liquid, from 1437 to 1595 K, again from a nickel container, the upper temperature limit being determined by the loss of strength of the nickel cell.

Masses corresponding to ThF_{4-n}, n = 0 to 4, were observed in the mass-spectrometric analysis, with ThF_4 being predominant. As for similar materials, the lower fluorides were attributed to fragmentation in the mass-spectrometer. There was no evidence for polymeric species.

These data have been processed by second and third-law methods in Section VIII.1.1.2.2.

[1958LEF]

Lefèbvre [1958LEF] reinterpreted potentiometric data from [1954HIE] and [1954KRA/HOL] in 1 M $NaClO_4$. Using his own calculation program, the author proposed the following complexes and equilibrium constants (given without uncertainties): $\log_{10}{}^*\beta_{2,1}(\mathrm{Th(OH)}_2^{2+}) = -7.47$, $\log_{10}{}^*\beta_{2,2}(\mathrm{Th}_2(\mathrm{OH})_2^{6+}) = -4.56$ and $\log_{10}{}^*\beta_{12,5}(\mathrm{Th}_5(\mathrm{OH})_{12}^{8+}) = -29.5$. For $\overline{n}_{\mathrm{OH}} > 2.3$ he claimed the predominance of a heptanuclear complex $\mathrm{Th}_7(\mathrm{OH})_n^{28-n}$ with n between 18 and 21.

The paper [1958LEF] does not contain new experimental data and the proposed speciation scheme and equilibrium constants are not accepted by this review. The potentiometric data of [1954HIE] and [1954KRA/HOL] have been evaluated subsequently by Baes *et al.* [1965BAE/MEY] and Hietanen and Sillén [1968HIE/SIL] who found a consistent model and equilibrium constants for the hydrolysis of thorium in 1 M $NaClO_4$ solution. Their model, including the complexes (*n,m*) = (1,1), (2,1), (2,2), (8,4) and (15,6), is selected in the present review.

[1958MAI/FOM]

Tributyl phosphate in benzene was used to extract thorium from aqueous solutions of 1.7 molar ionic strength containing H^+, NO_3^-, HSO_4^-, Na^+, and ClO_4^-. The required concentration of nitrate was obtained by $NaNO_3$, H^+ by $HClO_4$ and the ionic strength by the addition of $NaClO_4$. Two series of experiments were made with the total concentration of H^+ equal to 0.3 and 1.7 M, respectively; the HSO_4^- concentration ranged up to 0.05 M and that of nitrate up to 1.7 M. The temperature of the extractions is not reported.

The authors provide detailed information on the graphical methods used to deduce stoichiometry and equilibrium constants of the complexes formed in this ternary system and also experimental distribution coefficients. As discussed in [1956FOM/MAI] the authors have not taken the co-extraction of ClO_4^- and NO_3^- into the organic phase into account and the nitrate data are therefore unreliable. As sulphate is not co-extracted into the organic phase and the variation in the concentration of perchlorate is small, the activity of the species in the organic phase will be nearly constant and the experiments thus provide reliable information on the equilibrium constants of the sulphate complexes. The analysis of the experimental data is satisfactory. The nitrate system has been described assuming constant activity coefficients where the Th^{4+}- NO_3^- interactions are described using four complexes $\mathrm{Th(NO_3)}_n^{4-n}$. As discussed in this review, this does not provide a unique model in systems where weak complexes are formed and where the ionic composition of the test solutions have been varied significantly in the course of the experiment.

The authors calculated values of equilibrium constants for several reactions reported in the Table A-20.

Table A-20: Values of equilibrium constants at 1.7 M ionic strength.

Reaction	$\log_{10} K$
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	2.30
$Th^{4+} + 2\ HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2\ H^+$	3.40
$Th^{4+} + HSO_4^- + NO_3^- \rightleftharpoons Th(NO_3)(SO_4)^+ + H^+$	3.29
$Th^{4+} + HSO_4^- + 2\ NO_3^- \rightleftharpoons Th(NO_3)_2(SO_4)(aq) + H^+$	3.04
$Th^{4+} + HSO_4^- + 3\ NO_3^- \rightleftharpoons Th(NO_3)_3(SO_4)^- + H^+$	2.70

Assuming that the data presented by these authors pertain to 25°C and that we can use the SIT parameters given below as an estimate for the description of the ion interactions in the mixed ($HClO_4$)-(H,Na)NO_3 ionic medium (1.7 M or 1.85 m), this review calculated the values of $\log_{10} {}^*\beta_n^\circ$ with the SIT model from the $\log_{10} {}^*\beta_n$ reported by [1958MAI/FOM] using the relationship $\log_{10} {}^*\beta_n^\circ = (\log_{10} {}^*\beta_n - \Delta z^2 D + \Delta\varepsilon I_m) \pm (\sigma\Delta\varepsilon I_m)$. The SIT ion interaction parameters used in these calculations included $\varepsilon(Th^{4+}, ClO_4^-) \approx \varepsilon(H^+, HSO_4^-) = (0.70 \pm 0.10)$, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$, and $\varepsilon(ThSO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)\ kg{\cdot}mol^{-1}$ (for details about the selection of these parameters see Section IX.1.3.2). The $\log_{10} {}^*\beta_1^\circ$ and $\log_{10} {}^*\beta_2^\circ$ values for the binary sulphate system thus determined are (4.29 ± 0.27) and (5.75 ± 0.21). These $\log_{10} {}^*\beta_n^\circ$ values are very close to the values calculated from several other sources (*e.g.* [1959ZIE], [1951ZEB/ALT], [1972PAT/RAM]) and are accepted by this review.

The suggested composition and equilibrium constants for the ternary complexes are strongly dependent on the model used to describe the ion interactions and these data are not accepted by this review.

[1959GAG/MAS2]

These authors prepared various hydrates of thorium fluoride by precipitation from nitrate solutions using HF(aq), followed by controlled thermal treatment. Although full analysis of the samples was mentioned, no detailed analytical results were given. It was shown by these authors that careful vacuum dehydration of their samples up to 523 K did not alter their structure, as shown by their X-ray diffraction patterns and that they could be easily hydrated back to their initial water content. Examples found in the literature of hydrates with a similar behaviour are given. They measured calorimetrically the enthalpies of rehydration of the (presumably metastable) anhydrous ThF_4(cr) phases obtained by dehydration of $ThF_4{\cdot}2.5H_2O$(cr) and of $ThF_4{\cdot}0.5H_2O$(cr). These enthalpies of rehydration were reported to be $-(8.673 \pm 0.017)$ and $-(4.912 \pm 0.021)$ kJ·mol^{-1}, respectively.

It is interesting to note that in an adjacent paper [1959GAG/MAS], the same authors report a value of $-(25.48 \pm 0.05)$ kJ·mol^{-1} for the enthalpy of hydration of UF_4(cr) to $UF_4·0.4H_2O$(cr).

[1959HIE/SIL2]

The study has been made in a "self-medium", where the ionic medium cation consists of Th^{4+}. The experiments, potentiometric titrations have been made in test solutions of varying total concentration of protons, H_{tot}, in a $-\log_{10}[H^+]$ range where the value of $\bar{n}_{OH}$ is less than 0.1. Hence, the free metal ion concentration is approximately equal to Th_{tot} and it is straightforward to make the necessary corrections for the amount of hydroxide complexes formed. From experiments of this type it is only possible to determine the sum of the concentrations of Th complexes that contain a given number of hydroxide ions (one and two in this study); it is not possible to determine the nuclearity of the complexes without additional information. The experimental data obtained refers to reactions of the type

$$Th^{4+} + nH_2O(l) \rightleftharpoons \text{“}Th(OH)_n\text{”} + nH^+$$

where "[Th(OH)$_n$]" = $\sum m[\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}]$, the summation over m being from m = 1 to N (where N is the highest value for the nuclearity) for a given value of n.

In the present study, Hietanen and Sillén provide convincing evidence for the formation of complexes containing one and two coordinated hydroxides. By using additional information on the equilibrium constants for the mononuclear hydroxide complexes of Th(IV) they suggest that the complexes formed are binuclear, that is $Th_2(OH)^{7+}$ and $Th_2(OH)_2^{6+}$. The equilibrium constants for these complexes at 25°C are: $\log_{10}{}^*\beta_{1,2} = -(2.8 \pm 0.2)$ and $\log_{10}{}^*\beta_{2,2} = -(5.02 \pm 0.04)$ in 0.5 M $ThCl_4$; $\log_{10}{}^*\beta_{1,2} = -(2.9 \pm 0.2)$ and $\log_{10}{}^*\beta_{2,2} = -(5.09 \pm 0.04)$ in 0.7 M $ThCl_4$ + 2.2 M NaCl. The experimental technique and data analysis are described in detail. It is not possible to extrapolate the equilibrium constants to zero ionic strength and therefore no constants have been selected by this review.

[1959HIG]

Higashi measured the solubility of thorium hydroxide at room temperature from the direction of oversaturation. Thorium nitrate solutions (3×10^{-3} M, pH 2.5) were titrated with 0.1 M NaOH to pH values in the range 4 − 8. After precipitation of $Th(OH)_4$(s), the Th concentration and pH were measured after 30 minutes, 12 hours, 1, 2, 3, 7, 15, 30 and 100 days. No ionic medium was used in the experiments and the pH was measured using a glass electrode, but with no information about calibration procedures. Thorium concentrations were measured by a colorimetric method after filtration through filter paper, which is not sufficient to remove the colloidal and large polynuclear species $Th_m(OH)_{4m}(aq)$.

The author refers to the literature available at the time concerning the formation of Th(IV) hydroxide complexes, but does not use this information for the interpretation of the experimental data. It is obvious from Figure 4 in [1959HIG] that the reaction

$$Th(OH)_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4H_2O(l)$$

alone cannot describe the experimental data as also recognised by the author. For the quantitative evaluation of the Higashi's data it is helpful that the titration of 3×10^{-3} M $Th(NO_3)_4$ solutions with 0.1 M NaOH from pH 2.5 to 4 − 8 leads to $Th(OH)_4$ suspensions at approximately constant ionic strength, $I = 0.01$ M ($NaNO_3$). Assuming that the pH values given by the authors refer to the activity scale, this review converts pH into H^+ concentrations ($\log_{10}[H^+]$) with the activitity coefficient of $\log_{10}\gamma_{H^+} = -0.04$ calculated with the SIT for $I = 0.01$ M. Using the hydrolysis constants and ion interaction coefficients selected in this review, the solubility measured after 1 − 7 days corresponds to solubility constants $\log_{10} {}^*K^\circ_{s,0}$ decreasing from 10.0 to 9.0. Re-evaluation of the data measured after 100 days (solid line in Figure A-11) yields $\log_{10} {}^*K^\circ_{s,0} = (8.7 \pm 0.4)$ and $\log_{10} K_{s,(4m,m)} = -(6.8 \pm 0.2)$ for the reaction:

$$Th(OH)_4(am) \rightleftharpoons (1/m)\, Th_m(OH)_{4m}(aq).$$

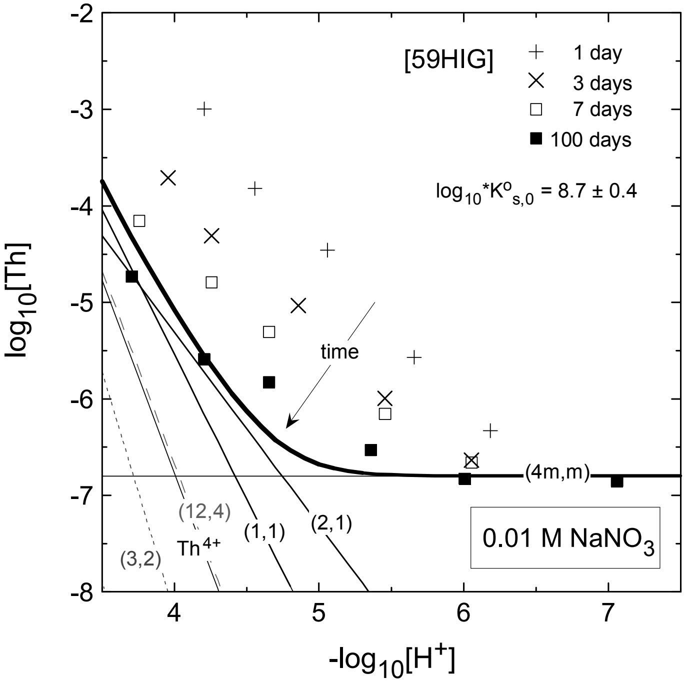
These two values are in reasonable agreement with the equilibrium constants recalculated by this review from numerous more recent data in chloride and perchlorate media. The results of [1959HIG] clearly demonstrate the very large effect of ageing as shown in Figure A-11 for the data measured after 1, 3, 7, and 100 days. This effect is more pronounced at lower pH and higher Th concentrations in solution. Ascribing the effect of ageing to an increase of particle size, due to recrystallisation *via* solution (dissolution-precipitation equilibria), explains that the increase of particle size is enhanced by the higher Th concentrations at low pH. This also indicates that the solubility data at different time and pH do not refer to a phase with a well-defined molar Gibbs energy.

[1959KIN/WEL]

This report describes heat-capacity measurements between 53 and 296 K for a sample of $ThS_2(cr)$, for which the analyses gave Th = 78.54 wt%, S = 21.43 wt%, corresponding to a composition of $ThS_{1.974}$. The heat capacity was extrapolated to 298.15 K to give $C^\circ_{p,m}(ThS_2, cr, 298.15\ K) = (70.29 \pm 0.50)\ J\cdot K^{-1}\cdot mol^{-1}$. The standard entropy was calculated to be $S^\circ_m(ThS_2, cr, 298.15\ K) = (96.23 \pm 1.70)\ J\cdot K^{-1}\cdot mol^{-1}$, where the heat capacity was extrapolated from 53 to 0 K using a combination of Einstein and Debye functions.

Similar measurements were made on samples of CeS(cr) and $Ce_2S_3(cr)$ which do not concern this review.

Figure A-11: Solubility of thorium hydroxide determined by Higashi [1959HIG] from oversaturation after 1, 3, 7, and 100 days. The calculated lines are based on the hydrolysis constants and ion interaction coefficients selected in this review, $\log_{10}{}^{*}K^{\circ}_{s,0} = 8.7$, and $\log_{10} K_{s,(4m,m)} = -6.8$.



[1959MIT2]

The heat capacities of Th, U, Be, Na and a Pb-Bi alloy were determined from 323 to 973 K by two methods, the precise details of which are not clear. For thorium (99.81% purity), two measurements were made at 323 and 373 K by comparing the cooling rate with an unspecified standard, and ten measurements from 523 to 973 K in an electron radiation calorimeter. The uncertainties in the values were estimated by the author to be 1.5−2%.

The derived heat capacity values have an unusually high temperature coefficient and since there are many other, better documented data, these results have not been included in the data fitting.

[1959PET/WES]

The solubility of hydrogen in Th(cr) was examined from 573 to 1073 K by equilibration of saturated samples and subsequent analysis. The solubility increased from about

1 atom% at 573 K to about 20 atom% at 1073 K, being given by the expression $\log_{10}(\text{atom\% H}) = -1732/T + 2.966$ for crystal bar thorium metal (main impurities: 170 ppm C, 200 ppm O and 135 ppm Fe).

[1959TAN/LU4]

A solution with constant $Th(NO_3)_4$ concentration of 0.0251 M was mixed with different concentrations of NaF at (25 ± 0.1)°C to obtain molar ratios of F to Th of 1 to 10. The solubility and solid phase characterisations of the resulting precipitates were investigated at pH values ranging from 2.52 to 6.30. The solubility results are presented in a tabular form. The authors did not detect any soluble Th at F:Th ratios of > 4.0 and the aqueous Th concentrations at F:Th ratios of < 1.5 are very similar to the Th added initially. The authors report the presence of colloids at F:Th ratios of < 3.8. The authors do not report any thermodynamic data, nor can any thermodynamic data be calculated because of the paucity of data points (only 4 points), lack of evidence for the presence of solid phase, and of equilibrium in this system. However, the authors provide convincing evidence, based on chemical, thermogravimetric, and X-ray diffraction analyses, that the compound that precipitates at higher NaF concentrations is $NaThF_5 \cdot H_2O$.

[1959TAN/LU5]

The authors used test solutions consisting of $Th(NO_3)_4$ or mixtures of $Th(NO_3)_4$ and NaF to increase the solubility of $CaF_2(s)$. From the measured solubility they could then determine the equilibrium constants for the fluoro complexes of Th(IV). The ionic strength of the solutions was not controlled and varied from about 0.1 to 5 M. No evidence is presented as to whether equilibrium is attained, or not. The number of data points on which the thorium fluoro complexes are based is very limited. The data reported by the authors correspond to average values of $\log_{10} K_1 = 5.92$ and $\log_{10} K_2 = 8.68$ for the reactions $Th^{4+} + F^- \rightleftharpoons ThF^{3+}$ and $Th^{4+} + 2F^- \rightleftharpoons ThF_2^{2+}$ respectively and for reasons stated above, these values are not accepted by this review.

[1959TAN/LU6]

This paper describes the aqueous concentrations and solid phases observed upon addition of KF or NH_4F to solutions of 0.0025 M $Th(NO_3)_4$ at 25°C. The concentrations of KF or NH_4F varied from 0.0025 to 0.025 M. The authors report Th, F, pH, and specific conductance in a tabular form and also report chemical compositions and XRD data. Their data indicate the presence of similar compounds in both the K and NH_4 fluoride systems and report the formation of normal thorium fluorides (ThF_4) and complex double salts of the type MTh_2F_9 and M_2ThF_6 with the progressive increase in F concentrations in relation to $Th(NO_3)_4$. The authors neither report any thermodynamic constants nor can any such data be extracted from this study due to the difficulties similar to those discussed under the other studies reported by these authors ([1959TAN/LU4], [1959TAN/LU5]).

[1959ZIE]

The equilibrium constants for the reactions:

$$\mathrm{Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+} \qquad \text{(A.35)}$$

$$\mathrm{Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+} \qquad \text{(A.36)}$$

have been determined at ionic strength 2.00 M using two different total concentrations of H^+, 1.00 and 2.00 M. The experiments were made using cation exchange at 25°C. At 1.00 M H^+ the test solutions were a mixture of $HClO_4$, H_2SO_4 and $NaClO_4$; at 2.00 M H^+ the test solutions were a mixture of $HClO_4$ and H_2SO_4. The total concentration of Th was around 10^{-5} M. The ion-exchange data were properly evaluated by assuring constant activity factors of the sorbed species by working at a constant load of the ion exchanger and taking both the sorption of Th^{4+} and $ThSO_4^{2+}$ into account. The data analysis indicated that the sorption of $ThSO_4^{2+}$ was negligible.

Zielen reports the following equilibrium constants for reactions (A.35) and (A.36):

$$K(\text{(A.35), 1.00 M H}^+) = (167 \pm 9);\ K(\text{(A.36), 1.00 M H}^+) = (3.63 \pm 0.21) \times 10^3;$$

$$K(\text{(A.35), 2.00 M H}^+) = (164 \pm 18);\ K(\text{(A.36), 2.00 M H}^+) = (3.49 \pm 0.44) \times 10^3.$$

These constants and their reported uncertainty at the 95% confidence limit are accepted by this review.

Zielen makes a comment on the formation of the complex $Th(SO_4)(HSO_4)^+$ suggested in [1951ZEB/ALT] and concludes that their data provide no evidence for the formation of this species; the present review agrees with this conclusion.

In a set of calorimetric experiments Zielen has determined the enthalpy of reaction for (A.35) and (A.36), together with the enthalpy of protonation of SO_4^{2-}. In order to evaluate the latter, Zielen used a dissociation constant of 0.084 for HSO_4^- from [1951ZEB/ALT]; this value is in fair agreement with the value 0.078 calculated at ionic strength 2.00 using the equilibrium constant and the ionic interaction coefficients selected in the NEA-TDB reviews. The proper corrections for heats of dilution and bulb breaking have been made in the calorimetric experiments. No test of the accuracy of the calorimetric procedure was made. However the measured enthalpy of protonation of sulphate, (5.54 ± 0.17) kcal·mol^{-1} ((23.18 ± 0.71) kJ·mol^{-1}) is in good agreement with the value 23.44 kJ·mol^{-1}, calculated from the enthalpy of formation of SO_4^{2-} and HSO_4^- selected in the NEA-TDB reviews. The experimental enthalpy of reaction for (A.35) and (A.36) from [1959ZIE]:

$$\Delta_r H_m(\text{(A.35), 298.15, } I = 2\text{ M}) = -(2.26 \pm 0.21)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_m(\text{(A.36), 298.15, } I = 2\text{ M}) = -(5.98 \pm 0.39)\ \text{kJ·mol}^{-1}$$

are accepted by this review.

This review calculated the values of $\log_{10}\, {}^{*}\beta_n^{\circ}$ at 25°C with the SIT model from the $\log_{10}\, {}^{*}\beta_n^{m}$ reported by [1959ZIE] using the relationship:

$$\log_{10}\, {}^{*}\beta_n^{\circ} = (\log_{10}\, {}^{*}\beta_n^{m} - \Delta z^2 D + \Delta\varepsilon I_m) \pm (\sigma\Delta\varepsilon I_m).$$

The SIT ion interaction parameters used in these calculations included $\varepsilon(\text{Th}^{4+}, \text{HSO}_4^-) \approx \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10)$, $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02)$, and $\varepsilon(\text{ThSO}_4^{2+}, \text{ClO}_4^-) = (0.3 \pm 0.1)\ \text{kg·mol}^{-1}$ (for details about the selection of these parameters see Section IX.1.3.2). The $\log_{10}\, {}^{*}\beta_1^{\circ}$ (A.35) and $\log_{10}\, {}^{*}\beta_2^{\circ}$ (A.36) values thus determined are (4.15 ± 0.32) and (5.76 ± 0.25). These $\log_{10}\, {}^{*}\beta_n^{\circ}$ values are very similar to the values calculated from several other sources (*e.g.*, [1958MAI/FOM], [1951ZEB/ALT], [1972PAT/RAM]) and were used in deriving the final value selected in this review for these reactions. The experimental Th concentrations at different sulphate concentrations are compared in Table A-21 with the concentrations predicted by the aqueous phase model selected in this review (see Section IX.1.3.2).

Table A-21: Observed [1959ZIE] and predicted concentrations at 25°C for ion-exchange studies in 2.2 m HClO_4-H_2SO_4 media (data are plotted in Figure IX-3). Predicted concentrations are based on NONLINT-SIT modeling calculations using the thermodynamic data reported in Tables IX-2 and IX-5.

Experimental data (m)				Model predictions (m)				
H^+	SO_4^{2-} total	ClO_4^-	Th total	Th total	Th^{4+}	ThSO_4^{2+}	$\text{Th(SO}_4)_2\text{(aq)}$	$\text{Th(SO}_4)_3^{2-}$
2.204	1.173×10^{-3}	2.203	3.735×10^{-9}	3.514×10^{-9}	3.212×10^{-9}	2.987×10^{-10}	2.794×10^{-12}	0
2.204	2.358×10^{-3}	2.202	3.982×10^{-9}	3.824×10^{-9}	3.212×10^{-9}	6.007×10^{-10}	1.129×10^{-11}	0
2.204	4.716×10^{-3}	2.199	4.723×10^{-9}	4.461×10^{-9}	3.213×10^{-9}	1.203×10^{-9}	4.512×10^{-11}	1.150×10^{-13}
2.204	7.074×10^{-3}	2.197	5.008×10^{-9}	5.123×10^{-9}	3.213×10^{-9}	1.808×10^{-9}	1.015×10^{-10}	3.880×10^{-13}
2.204	9.432×10^{-3}	2.195	5.651×10^{-9}	5.808×10^{-9}	3.213×10^{-9}	2.414×10^{-9}	1.805×10^{-10}	9.197×10^{-13}
2.204	1.178×10^{-2}	2.193	6.909×10^{-9}	6.518×10^{-9}	3.213×10^{-9}	3.021×10^{-9}	2.819×10^{-10}	1.794×10^{-12}
2.204	2.244×10^{-2}	2.182	1.012×10^{-8}	1.004×10^{-8}	3.215×10^{-9}	5.793×10^{-9}	1.022×10^{-9}	1.239×10^{-11}
2.204	4.496×10^{-2}	2.161	1.939×10^{-8}	1.920×10^{-8}	3.217×10^{-9}	1.178×10^{-8}	4.101×10^{-9}	9.959×10^{-11}
2.204	5.609×10^{-2}	2.150	2.523×10^{-8}	2.460×10^{-8}	3.218×10^{-9}	1.481×10^{-8}	6.379×10^{-9}	1.933×10^{-10}
2.204	6.733×10^{-2}	2.139	3.019×10^{-8}	3.064×10^{-8}	3.219×10^{-9}	1.790×10^{-8}	9.191×10^{-9}	3.344×10^{-10}
2.204	7.845×10^{-2}	2.129	3.799×10^{-8}	3.725×10^{-8}	3.220×10^{-9}	2.102×10^{-8}	1.248×10^{-8}	5.289×10^{-10}
2.204	8.991×10^{-2}	2.118	4.349×10^{-8}	4.468×10^{-8}	3.222×10^{-9}	2.427×10^{-8}	1.639×10^{-8}	7.961×10^{-10}
2.204	1.009×10^{-1}	2.107	4.862×10^{-8}	5.245×10^{-8}	3.223×10^{-9}	2.745×10^{-8}	2.065×10^{-8}	1.126×10^{-9}
2.204	1.122×10^{-1}	2.096	5.749×10^{-8}	6.102×10^{-8}	3.224×10^{-9}	3.074×10^{-8}	2.551×10^{-8}	1.547×10^{-9}
2.204	1.683×10^{-1}	2.042	1.102×10^{-7}	1.136×10^{-7}	3.230×10^{-9}	4.784×10^{-8}	5.733×10^{-8}	5.214×10^{-9}
2.204	2.243×10^{-1}	1.989	1.796×10^{-7}	1.836×10^{-7}	3.236×10^{-9}	6.620×10^{-8}	1.018×10^{-7}	1.235×10^{-8}

There is a close agreement between the predicted and the experimental data. Graphical comparisons are presented in Figure IX-3, Section IX.1.3.2.

[1960DAN]

The author has measured the distribution of trace amount of Th(IV) between an aqueous phase and a nitrate-loaded anion exchanger to determine equilibrium constants in the Th(IV)-nitrate system. The method used to evaluate the experimental data are from Marcus and Coryell [1959MAR/COR]. The experimental study was made by measuring the distribution coefficient for Th(IV) between an ion-exchanger and test solutions in which the concentration of $LiNO_3$ was varied between 1.55 and 8.44 M; there is no information on the temperature at which the experiments were performed. The ionic strength of the test solutions is not constant and the activity coefficients of reactants and products will therefore vary; the variation in the (single-ion) activity coefficient of NO_3^- has been assumed to be the same as the mean activity coefficient of $LiNO_3$. When the concentration of the $LiNO_3$ in the aqueous phase varies, the invasion of $LiNO_3$ into the ion exchanger will vary, leading to different concentrations (and activity) of $LiNO_3$ in the resin phase, a factor that also must be taken into account when evaluating the experimental data (the method to do this is from Marcus and Coryell).

The net result of the experimental study is a distribution curve $\log_{10}D$ *vs* the activity of NO_3^-, a curve that has a maximum where the concentration of the uncharged complex $Th(NO_3)_4(aq)$ has its maximum value. The decrease of $\log_{10}D$ at lower nitrate concentration is due to the dissociation of the uncharged complex to form cationic complexes; the decrease at higher nitrate concentrations to the formation of anionic complexes. The experimental method is accordingly very similar to the measurement of the distribution of an uncharged complex between an aqueous and an organic phase. The important difference is that the control of the activity factors is much more difficult in the anion exchange method.

Danon reports equilibrium constants for the following reactions:

$$Th(NO_3)_4(aq) \rightleftharpoons Th(NO_3)_3^+ + NO_3^- \quad \log_{10}K = 0.22$$

$$Th(NO_3)_4(aq) + NO_3^- \rightleftharpoons Th(NO_3)_5^- \quad \log_{10}K = -(0.80 \pm 0.17)$$

$$Th(NO_3)_4(aq) + 2NO_3^- \rightleftharpoons Th(NO_3)_6^{2-} \quad \log_{10}K = -(1.70 \pm 0.22).$$

Danon points out that the data can also be described with a model where no cationic complexes are formed. The key conclusion of this study is that the uncharged complex $Th(NO_3)_4(aq)$ is predominant when the activity of the nitrate is about 0.5 M and that anionic complexes are formed at higher nitrate activities. In the analysis of the experimental data, Danon has not considered the variation of the activity coefficients of the thorium species participating in the reactions and there is no justification for this approximation. Because of this, the present review has not accepted the equilibrium constants proposed by Danon. It should be noted that the experimental mean-activity coefficients of thorium nitrate solutions can be well described by the simple SIT model without any assumptions of complexes up to nitrate concentrations of 3.5 m ([2006NEC/ALT], see Figure X-1). However, there is structural evidence for the formation of nitrate coordination, *cf.* Section X.1.3.3 and [1968JOH], [1968JOH2], [1991JOH/MAG].

[1960DAR]

The equilibrium pressures of SiF_4 for the reaction:

$$ThF_4(cr) + SiO_2(cr) \rightleftharpoons ThO_2(cr) + SiF_4(g)$$

were measured from 871 to 1077 K.

$ThF_4(cr)$ was purified by heating *in vacuo* at 873 K for 16 h, giving material with 75.3 and 25.4 wt% Th and F, as compared with the theoretical values of 75.33 and 24.67. Finely particulate SiO_2 was prepared from $SiF_4(g)$ and fired at 1073 K. ThO_2 powder of 99.8 wt% purity was heated to 973 K *in vacuo.*

Seventeen measurements were made on hydraulically pressed mixtures of equimolar amounts of $ThF_4(cr)$ and $SiO_2(cr)$, broken into *ca.* 1 mm cubes, and gave equilibrium pressures of $SiF_4(g)$ in 2 − 4 h. There was satisfactory agreement between the pressures approached from pressures higher and lower than the equilibrium value.

There are two minor problems with interpreting these data. Firstly, the polymorph of silica involved in the reaction is unknown. However, the Gibbs energies of formation of the polymorphs of silica do not differ greatly and we have taken the phases to be α- or β-quartz (although it is more likely to have been an amorphous form) and increased the uncertainty of the derived enthalpy of formation.

A more serious problem is that $ThF_4(cr)$ and $SiO_2(cr)$ are not the equilibrium phases in this system, since $ThOF_2(cr)$ is a stable phase, although its preparation needs temperatures of 1173 − 1273 K. Darnell in fact found traces of $ThOF_2(cr)$ in his quenched samples. However, the pressures in two measurements of the reverse reaction (ThO_2 reacting with $SiF_4(g)$) were in good accord with those of the forward reaction. Moreover, Darnell also measured the pressures in the reaction of SiO_2 and $ThOF_2(cr)$ (presumably from the reaction $2ThOF_2(cr) + SiO_2(cr) \rightleftharpoons 2ThO_2(cr) + SiF_4(g)$) which are lower than those in the current study. However, these data are not quoted by the author.

The reaction involved was thus probably that postulated by the author, $ThOF_2(cr)$ not being formed for kinetic reasons. The data have been processed by the third-law method to give a value for $\Delta_f H_m$ (ThF_4, cr, 298.15 K).

[1960DAR2]

The equilibrium pressure of ThF_4 from the decomposition of $ThOF_2$ was measured in a Knudsen effusion cell from 1109 to 1286 K. The $ThOF_2$ was prepared by heating a mixture of fine ThO_2(cr) and ThF_4(cr) powders to 1173 K in an argon atmosphere for 16 h. The decomposition pressures were only about a factor of two smaller than the vapour pressure of pure ThF_4(cr) measured by the same authors [1958DAR/KEN], and agree excellently with those measured more recently by Lau *et al.* [1989LAU/HIL]. The results were processed by the second-law to give the enthalpy of formation and standard entropy of the oxyfluoride. The oxyfluoride is only marginally stable with respect to ThO_2(cr) and ThF_4(cr).

[1960DAR/MCC]

The vapour pressure of Th(cr) was measured at 1757 − 1956 K by the Langmuir method. Special purification of the thorium was necessary since traces of ThO_2 react with Th to give ThO(g). The vapour pressure equation is $\log_{10} p(\mathrm{Th})/\mathrm{bar} = -(28780 \pm 620)/T + (5.997 \pm 0.333)$.

This is a good study which recognised the importance of ThO(g) in the vaporisation even of nominally high purity thorium, before the application of mass-spectrometry to such systems. Residual oxygen in the vacuum system is also gettered by Th(cr) to form ThO(g). Darnell *et al.* attempted to reduce the oxygen contamination (initially ~ 1000 ppm) of their sample by volatilisation of ThO(g) for 200 h at 1883 K; however their sample still contained 30 ppm oxygen, and subsequent work by Ackermann and Rauh [1972ACK/RAU] suggest that their measured pressures are too high by about a factor of three, due to residual ThO(g) in the vapour. Second and third-law analyses of their data by this review give $\Delta_f H^\circ_m$ (Th, g, 298.15 K) = (561.5 ± 23.7) $\mathrm{kJ \cdot mol^{-1}}$ and (581.5 ± 5.0) $\mathrm{kJ \cdot mol^{-1}}$ respectively, somewhat lower than the selected value, owing to the presence of ThO(g) in the vapour.

[1960FIL/TEK]

The solubility of ThP_2O_7(s) at 20ºC was determined in solutions of $Na_4P_2O_7$ and also in three acid solutions, by using a radioactive thorium tracer. The solid phase was characterised by elemental analysis prior to the equilibration and also after equilibrium had been attained.

In one set of experiments the authors measured the solubility as a function of the total concentration of HCl, HNO_3 and H_2SO_4, respectively. For a variation of the total concentrations of acid in the range 0.1 − 0.5 M the solubility varied between 4×10^{-4} and 8×10^{-4} M in the sulphuric acid system; between 0.5×10^{-4} and 5×10^{-4} M in the nitric acid system and between 0.1×10^{-4} and 2×10^{-4} M in the hydrochloric acid system. As the chloride and nitrate complexes of Th(IV) are weak one would not expect that the solubility would be systematically different in these two systems. The solubility in the sulphuric acid is only a factor of two larger than the solubility in the nitrate system and here one would expect a larger difference because of the strong sulphate complexation. The authors have not made any attempt to calculate the solubility product of the solid. The experiments in the $Na_4P_2O_7$ test solutions were made at four different total concentrations of $Na_4P_2O_7$ of 0.0237, 0.0475, 0.0055 and 0.2040 M, but with no information on the pH in the test solutions used; the measured solubility in these solutions was 0.0205, 0.0433, 0.0320 and 0.0077 M, respectively. The variation in the solubility is small, the pH unknown and it is therefore not possible to determine a solubility product from these data. The measured solubility in [1960FIL/TEK] differs very significantly from that obtained in [1967MER/SKO], in 0.1 M $HClO_4$. Filinov *et al.* observed that a mixed solid phase consisting of $Th_2P_2O_7(s)$ and $Na_4Th(P_2O_7)_2(s)$ is formed at concentrations of $Na_4P_2O_7$ higher than 0.0475 M. The authors compared conductivity measurements in pure $Na_4P_2O_7$ solutions and test solutions of $Na_4Th(P_2O_7)_2$ and derived an "approximate" equilibrium constant of $\log_{10} K = -(5.25 \pm 0.17)$ for the dissociation of $Th(P_2O_7)_2^{4-}$ into $ThP_2O_7(aq)$ + $P_2O_7^{4-}$. This value corresponds to a stepwise complexation constant of $\log_{10} K_2 = (5.25 \pm 0.17)$ for the reaction:

$$ThP_2O_7(aq) + P_2O_7^{4-} \rightleftharpoons Th(P_2O_7)_2^{4-} .$$

They also note that the reaction takes place with a decrease of about 1.5 pH units. The present review suggests that this is an indication that ternary complexes containing hydroxide might be formed. The pH in the $Na_4P_2O_7$ test solutions vary between approximately 8.8 and 9.5 and in this range the concentration of protonated $H_xP_2O_7^{x-4}$ species is significant. These facts demonstrate that the stoichiometry of the complexes formed has not been ascertained and accordingly no equilibrium constants can be determined. The only conclusion to be drawn from this study is qualitative, that complexes are formed in the Th(IV)-pyrophosphate system.

[1960LAN/DAR]

Landis and Darnell [1960LAN/DAR] attempted to obtain the Gibbs energy of formation of $ThI_4(cr)$ by measuring the ‘equilibrium’ pressure of $TiI_4(g)$ in the reaction:

$$ThI_4(cr) + TiO_2(cr) \rightleftharpoons ThO_2(cr) + TiI_4(g)$$

from 637 to 745 K by Knudsen effusion. However, as with the similar reaction involving the fluorides (with silica), $ThI_4(cr)$ and $ThO_2(cr)$ can never coexist in true equilibrium. This effect is much more serious in the present case since $ThOI_2(cr)$ is quite stable with respect to decomposition to $ThO_2(cr)$ and $ThI_4(cr)$, whereas $ThOF_2(cr)$ is only just stable with respect to the similar decomposition. In fact, in the light of present knowledge on the stabilities of $ThI_4(cr)$ and $ThOI_2(cr)$ (see Sections VIII.4.1.2 and VIII.4.1.5) it is clear that the initial reaction between the reactants used:

$$2ThI_4(cr) + TiO_2(cr) \rightleftharpoons 2ThOI_2(cr) + TiI_4(g)$$

will have an equilibrium pressure in excess of one atmosphere even at room temperature. Thus $ThOI_2(cr)$ was probably formed during the initial heating and the reaction studied by Landis and Darnell was most likely

$$2ThOI_2(cr) + TiO_2(cr) \rightleftharpoons 2ThO_2(cr) + TiI_4(g) \qquad (A.37)$$

Their Gibbs energies near the centre of their temperature range are represented by the equation:

$$[\Delta_r G_m]_{640K}^{750K}\ ((A.37), T) = 208332 - 230.147\ T\ (J \cdot mol^{-1}).$$

The scatter in the experimental data is quite pronounced and the temperature range quite short, so these values have appreciable uncertainty. However, the derived enthalpy of reaction at 700 K, (208.3 ± 10.5) kJ·mol^{-1} overlaps, within the combined uncertainties, with that calculated for Reaction (A.37), (194.7 ± 10.4) kJ·mol^{-1}, assuming the heat capacity of $ThOI_2$(cr) is the mean of those of ThO_2(cr) and ThI_4(cr). The data have, therefore, been used to provide an estimate of the entropy of $ThOI_2$(cr) – see Section VIII.4.1.5.

[1960MAT/ABR]

This paper presents a different approach to study hydrolysis; the authors have used the well-known fact that the addition of metal ions to lyotropic colloids of AgI, AgBr and AgCl results in coagulation, where the coagulation point is determined by the charge of the metal ion (or a charged complex). The metallic ion concentration where coagulation takes place can be estimated from the turbidity of the test solutions. An important feature of this method is that only very small concentrations of metal ions are necessary; in this study the thorium concentrations are in the range 10^{-6} M. Matijević *et al.* noticed that the coagulation point varied with pH and ascribed this to a change in charge of the species causing the coagulation. At pH < 4 they suggested that the metal species had a charge of +4 and at pH around 7 a charge of +3. It is reasonable to assume that only mononuclear hydroxide complexes are formed at these low Th-concentrations and pH < 5. At low pH, the observations are consistent with proposed hydrolysis data, but not at high pH. At pH > 5 the Th concentration of 10^{-6} M exceeds the solubility of $Th(OH)_4$(am) by 1 – 2.5 orders of magnitude which result in the formation of approximately uncharged Th(IV) polymers/colloids which remain dissolved in solution (*cf.* [2004ALT/NEC]), if they are not sorbed on the container walls. This study does not provide quantitative information on equilibrium constants, but gives qualitative support for the formation of hydroxide complexes.

The authors also noticed that a reversal of charge of the colloids could take place, but not in test solutions containing Th^{4+}, only at higher pH where thorium hydroxide complexes were formed. This observation is important for the modelling of Th sorption on colloidal systems. For negatively charged colloids like AgI, AgBr and AgCl the presence of coordinated hydroxide groups seems to result in a strong sorption of positively charged thorium hydroxide complexes and accordingly charge reversal of the colloids.

[1960MAY/OWE]

Mayer *et al.* reported enthalpy increment data for $Th(SO_4)_2(cr)$ from 623 to 897 K, from which they derived the following heat capacity equation, assumed to apply down to 298.15 K:

$$[C_{p,\mathrm{m}}]_{298.15\mathrm{K}}^{900\ \mathrm{K}}(\mathrm{Th(SO_4)_2, cr}, T) = 104.6 + 23.096\times10^{-2}\ T \qquad (\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$$

These data have been adopted.

The authors also report the decomposition pressures for the reaction $Th(SO_4)_2(cr) \rightleftharpoons ThO_2(cr) + 2SO_2(g) + O_2(g)$ from 908 to 1057 K. Although Mayer *et al.* did not show that the $SO_2(g)/O_2(g)$ ratio was 2:1, to demonstrate unambiguously that the above equilibrium was in fact being studied, they did analyse the samples after the experiments and could not detect any solid solution or oxysulphate. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons SO_3(g)$ was established in the gas phase by the presence of a platinum coil in the gas stream. The equilibrium constants for the reaction calculated by the review, including the correction for the presence of the small amount of $SO_3(g)$, using values from Table IV-1 and [1989GUR/VEY], agree closely with those given in the paper. Lacking a reliable entropy value for $Th(SO_4)_2(cr)$, we are forced to utilise a second-law treatment of the data, recognising that the derived values must have considerable uncertainty owing to the small temperature interval. With the thermal data for $ThO_2(cr)$ from the present assessment and for $SO_2(g)$ and $O_2(g)$ from the Table IV-1, we finally derive the following values: S°_{m} ($Th(SO_4)_2$, cr, 298.15 K) = (146.3 ± 4.9) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($Th(SO_4)_2$, cr, 298.15 K) = $-(2543.2 \pm 4.9)$ $\mathrm{kJ{\cdot}mol^{-1}}$ and hence $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($Th(SO_4)_2$, cr, 298.15 K) = $-(2307.4 \pm 5.1)$ $\mathrm{kJ{\cdot}mol^{-1}}$. However, as discussed in Section IX.1.3.1, this Gibbs energy of formation corresponds to a very low (hypothetical) solubility of $Th(SO_4)_2(cr)$ to (predominantly) $Th(SO_4)_2(aq)$ and thus has not been selected by the review. The reason for the considerable discrepancy is not clear.

[1960MUH/VAU]

Aqueous solutions of $MOX_2{\cdot}8H_2O$, where M = Zr, Hf and X = Cl or Br have been studied using large angle X-ray scattering. The total concentrations of the test solutions were 0.5, 1.0, 1.5 and 2 m for $HfOCl_2$ and 2 molal for the remaining solutions. The radial distribution functions have been derived and used to deduce a structure model that is the same for all systems and consists of a square arrangement of metal ions, linked by double hydroxide bridges. The coordination number of the M^{4+} ions is eight, four bridging OH^- ions and four water molecules; the halide ions are located in the second coordination sphere. The M–M distance is 3.57 Å and the M–O distance 2.24 Å, the same as in crystalline $ZrOCl_2{\cdot}8H_2O$. The authors suggest a square antiprism geometry around M, this is chemically reasonable, but information of this type cannot be deduced from these experimental data. Because of the chemical similarity between Zr, Hf and Th, this study provides a model for the structure of tetranuclear $[Th_4(OH)_8]^{8+}$ hydroxide complex.

[1960WAL]

The heat capacity of high-purity thorium wires (*ca.* 150 ppm non-metallic elements) has been measured from room temperature to 1273 K, using an electrical pulse-heating method. The sample was held *in vacuo* in a furnace, at 1273 K, and cooled slowly at *ca.* 40 K·hr^{-1}, during which it was periodically pulsed electrically and the rate of temperature change monitored. The heat capacity was evaluated at about 25 data points for each of ten pulses used, but the only a table of the fitted values at round temperatures are given. The uncertainty in $C_{p,\mathrm{m}}$ is estimated by the authors to be 2% at most.

As noted in Section V.1.2 although these data agree well with one set of low-temperature data (by [1953GRI/SKO]) near room temperature, the results of subsequent measurements indicate that they are somewhat too high over the whole temperature range, and they have not been included in the data fitting.

[1960YOS]

In this Progress Report, Yosim reports preliminary details of a study of the decomposition pressure of ThI_4(g) above ThI_3(cr) and ThI_2(cr) (presumably, in practice, the {ThI_3(cr) + ThI_2(cr)} and {ThI_2(cr) + Th(cr)} diphasic fields). At an unspecified temperature, the pressures of ThI_4(g) above the two compounds/phase fields are reported to be 0.15 − 0.20 and 0.004 times the sublimation pressure of pure ThI_4(cr). He suggests that the results indicate that the Gibbs energy of formation of ThI_4(cr), ThI_3(cr), ThI_2(cr) per iodine atom are very similar, which would be consistent with the phase diagram of [1964SCA/WYL].

There is insufficient detail in the paper to derive any more quantitative data from this study

[1961BUC/BER]

Samples of ThF_4 and $ThCl_4$ were heated to 1475 and 950 K respectively to observe their infrared spectrum. The observed values of the stretching frequencies were 520 and 335 cm^{-1} respectively. The values for the zirconium and hafnium halides agreed closely with earlier measurements. The frequencies of the bending vibration, also active in the infrared, were lower than the cut-off (*ca.* 200 cm^{-1}) of the CsI prism used in the spectrometer.

[1961CAT/RAU]

In a mass-spectrometric study of the vapour effusing from a sample of US(cr) contained in tungsten, Cater *et al.* [1961CAT/RAU] tentatively attributed a weak peak at mass number 264 to ThS(g) from adventitious thorium impurity in the system.

[1961CHE/GOL2]

The paper describes the preparation of $[NH_4]_6[Th(CO_3)_5]\cdot 3H_2O$ and the characterisation of this phase; no thermodynamic data are reported.

[1961DAR/MCC]

The evaporation behaviour of the Th-O system was studied from 1984 to 2564 K, using mass-loss Knudsen effusion measurements on the dioxide phase and {liquid metal + dioxide} mixtures.

The thorium used was stated to be of 99.8% purity, but no details of the analysis are given. The mass effusion rate from ThO_2(cr) contained in a thoria-lined tungsten effusion cell was measured from 2268 to 2593 K (13 points) and from mixtures of Th(cr, l) and ThO_2(cr) from 1984 to 2564 K (35 points, rather scatted data). A mass-spectrometric study of the vaporisation from {Th(l) + ThO_2(cr)} mixtures from tungsten cells showed that the vapour was predominantly ThO(g), but at 2125 K, ion currents attributed to Th(g) were observed. The vaporisation of ThO_2(cr) was not apparently studied mass-spectrometrically, and the reaction was assumed to be simple vaporisation to ThO_2(g). The derived equations for the pressures were $\log_{10} p_{\mathrm{ThO_2(g)}}/\mathrm{bar} = -(22.210 \pm 680)/T + (4.69 \pm 0.31)$ from {Th(l) + ThO_2(cr)} mixtures (corrections were made for the calculated contributions of Th(g) and ThO_2(g) to the total pressure) and $\log_{10} p_{\mathrm{ThO_2(g)}}/\mathrm{bar} = -(35.460 \pm 1140)/T + (8.17 \pm 0.47)$ from ThO_2(cr).

The authors also determine the solubility of oxygen in Th(l), reporting values of 3.5 wt% ThO_2 at 2090 K and of 8.2 wt% ThO_2 at 2450 K. These values are reasonably consistent with the later data of Benz [1969BEN].

These data have been used by the review to calculate the Gibbs energies of formation of ThO(g) and ThO_2(g), by third-law processing. For ThO(g), the calculated value of $\Delta_f H_m^\circ$ (ThO, g, 298.15 K) is $-(28.6 \pm 23.3)$ kJ·mol^{-1}, where the uncertainty is the 2σ statistical value only. Inclusion of the experimental uncertainties is estimated to increase this to 23.5 kJ·mol^{-1}. For ThO_2(g), the calculated value of $\Delta_f H_m^\circ$ (ThO_2, g, 298.15 K) is $-(459.5 \pm 12.0)$ kJ·mol^{-1}, where the uncertainty is again the 2σ statistical value only. Inclusion of the experimental uncertainties is estimated to increase this to 15.0 kJ·mol^{-1}. But this value of $\Delta_f H_m^\circ$ (ThO_2, g, 298.15 K) does not take into account the fact that there are small amounts of ThO(g) and O(g) in the vapour, so will be slightly too low.

[1961HAR/MOO]

The authors report measurements of the enthalpies of combustion of UOS(cr), ThOS(cr), α-US_2(cr), and ThS_2(cr). ThOS(cr) and ThS_2(cr) were prepared from reaction of ThO_2(cr) in flowing H_2S(g) in a graphite crucible at 1773 K. Although they report that the powder diffraction data show no impurities and that the products were analysed using various methods, no details of these analyses are given. Also mentioned are the measurements of the average $C_{p,\mathrm{m}}$ values necessary for the calculation of the enthalpies of formation at 298.15 K. The $C_{p,\mathrm{m}}$ values reported for the thorium compounds are $[C_{p,\mathrm{m}}]^{773\mathrm{K}}_{298.15\mathrm{K}}$ (ThO_2, cr) = (74.1 ± 2.2) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $[C_{p,\mathrm{m}}]^{773\mathrm{K}}_{298.15\mathrm{K}}$ (ThOS, cr) = (76.6 ± 2.3) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, and $[C_{p,\mathrm{m}}]^{773\mathrm{K}}_{298.15\mathrm{K}}$ (ThS_2, cr) = (72.8 ± 2.2) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, where the authors' given uncertainties (1.5%) have been doubled. However, the selected data for ThO_2(cr), based on a number of consistent studies (see Section VII.1.2.2) give a mean heat capacity of 69.9 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ for this temperature range, so the authors may have underestimated their errors. It will be noted also that the mean heat capacities do not follow the sequence expected for a series of non-magnetic solids, $C^{\circ}_{p,\mathrm{m}}$ (ThO_2,cr) < $C^{\circ}_{p,\mathrm{m}}$ (ThOS, cr) < $C^{\circ}_{p,\mathrm{m}}$ (ThS_2,cr).

The following enthalpies of formation for the two thorium compounds are given without any details of the experimental results or method of calculation: $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThOS, cr, 298.15 K) = −(862 ± 26) $\mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThS_2, cr, 298.15 K) = − (816 ± 24) $\mathrm{kJ{\cdot}mol^{-1}}$. However, the value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThS_2, cr) is almost certainly too negative, since these values would indicate that the enthalpy of the decomposition reaction:

$$2\mathrm{ThOS(cr)} \rightleftharpoons \mathrm{ThO_2(cr)} + \mathrm{ThS_2(cr)} \qquad \text{(A.38)}$$

becomes $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((A.38), 298.15 K) = −(318 ± 57) $\mathrm{kJ{\cdot}mol^{-1}}$, using $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThO_2, cr, 298.15 K) = −(1226.4 ± 3.5) $\mathrm{kJ{\cdot}mol^{-1}}$ selected in this review. Since the entropy change in this all-solid reaction will be small, this would imply ThOS(cr) would never be easily formed from these solids (*cf.* [1984AMO/BLA2]). In view of these notable inconsistencies, the data of [1961HAR/MOO] are not considered in this review.

[1961HOC/JOH]

The enthalpies (referred to 0°C) of Al_2O_3 (corundum) and of ThO_2(cr) were determined in the range 1555 to 2278 and 1456 to 2753 K, respectively by drop calorimetry.

The sample of thoria used was the same as that used in the vapour pressure study [1954HOC/JOH] by the same authors. No further analysis is given. It was held in a tantalum container, with which "only very slight reaction was observed between ThO_2 and the tantalum holder".

Six measurements were made, extending from 1456 to 2753 K. They agree very well with other experimental data and were included in the data fitting.

[1961KOV/BAG2]

The solubility of $Th(OH)_4$(s) was measured at 22°C in test solutions of different pH adjusted in the range of 3 to 5 by adding HNO_3 to thorium hydroxide suspensions in water and 0.5 to 4 M KNO_3. After 24 hours of equilibration and phase separation by filtration or centrifugation (no further details given), thorium concentrations were measured colorimetrically using the organic reagent "thoron". No information is given on the determination of pH. The measured thorium concentrations were ascribed exclusively to

Th^{4+} without considering hydrolysis and the solubility product is calculated according to:

$$K_{sp} = [\mathrm{Th}^{4+}]\, K_{\mathrm{w}}{}^{4} \times 10^{4\mathrm{pH}}$$

as a function of pH and Th concentration. From the linear extrapolation of the $-\log_{10} K_{sp}$ values in water to [Th] = 0, the authors derived the solubility product at zero ionic strength $\log_{10} K^{\circ}_{sp} = -44.7$. Applying similar graphical procedures to the $-\log_{10} K_{sp}$ values determined in 0.5−4 M KNO_3 the authors obtained an average value of $\log_{10} K^{\circ}_{sp} = -44.0$.

The calculated solubility products are based on erroneous assumptions and inadequate extrapolation procedures and the primary experimental data are not given. Only the experimental data in the experiments without background electrolyte (varying ionic strength) are shown in Figure 3 of [1961KOV/BAG2]. However, this figure is too small to extract the data. Therefore no quantitative information can be drawn from this study. When the pH in the test solutions decreased from about 3.6 to 3.2, there was a sharp increase in the solubility of thorium to a maximum value of about 3.5 mM. A further decrease in pH to 2.2 did not result in any additional increase in solubility.

[1961LUZ/KOV2]

The solubility in the system Th-Na_2CO_3-H_2O has been studied as a function of the total concentration of Na_2CO_3 at 25°C using $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ as the initial solid phase. The molality of Na_2CO_3 varied from 0.79 to 2.8 mol·kg^{-1} and the concentration of dissolved Th and the composition of the solid phase in equilibrium with the solution were analysed. In the concentration range $0.79 < m_{\mathrm{Na_2CO_3}} < 2.4$ mol·kg^{-1} the data indicate that the only solid phase present is $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$; at higher carbonate concentrations solid Na_2CO_3 is also present. Luzhnaya and Kovaleva observed that the solubility of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ decreased with increasing carbonate concentration; the only possible reasons for this is the increase of the concentration of $[Na^+]$ and changes in the activity coefficients. This review has therefore used the experimental data to calculate the concentration product $[Na^+]^6\,[Th(CO_3)_5]$ using the experimental data in Table 1 of [1961LUZ/KOV2]. The solubility constant $\log_{10} K^{\circ}_{s,5}$ at zero ionic strength for the reaction:

$$\mathrm{Na_6[Th(CO_3)_5]\cdot 12H_2O(s)} \rightleftharpoons 6\mathrm{Na}^+ + \mathrm{Th(CO_3)_5^{6-}} + 12\mathrm{H_2O(l)} \qquad \text{(A.39)}$$

is calculated from the experimental data in 0.79−2.8 m Na_2CO_3 solution according to

$$\log_{10} K^{\circ}_{s,5} = 6\log_{10}[\mathrm{Na}^+] + \log_{10}[\mathrm{Th(CO_3)_5^{6-}}] - 42D + 6\,\varepsilon(\mathrm{Na}^+, \mathrm{CO_3^{2-}})\cdot m_{\mathrm{CO_3^{2-}}} + \varepsilon(\mathrm{Th(CO_3)_5^{6-}}, \mathrm{Na}^+)\cdot m_{\mathrm{Na}^+} + 12\log_{10} a_w \qquad \text{(A.40)}$$

with $\varepsilon(\mathrm{Na}^+, \mathrm{CO_3^{2-}}) = -(0.08 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(\mathrm{Th(CO_3)_5^{6-}}, \mathrm{Na}^+) = -(0.30 \pm 0.15)$ kg·mol^{-1}.

Table A-22: Evaluation of $\log_{10} K^{\circ}_{s,5}$ ($Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$) from the solubility data of [1961LUZ/KOV2] at (25.0 ± 0.1)°C.

Solution composition (wt%)			Molality m_i (mol·kg^{-1} H_2O)					
Na_2CO_3	$Th(CO_3)_5$	H_2O	Na_2CO_3	$Th(CO_3)_5^{6-}$	I_m	a_w	$\log_{10} K_{s,5}$	$\log_{10} K^{\circ}_{s,5}$ [c]
22.55 [a]	0.38	77.07	2.76	0.0093 [b]	8.48	0.904		
22.60 [a]	0.53	76.87	2.77	0.0130 [b]	8.59	0.904		
22.70 [a]	0.86	76.44	2.80	0.0211	8.85	0.903	2.87	– 12.36 ± 0.98 [d]
22.97 [a]	0.96	76.07	2.85	0.0237	9.04	0.902	2.97	– 12.35 ± 1.00 [d]
22.81 [a]	0.86	76.33	2.82	0.0212	8.90	0.903	2.89	– 12.38 ± 0.99 [d]
20.02	1.01	78.98	2.39	0.0240	7.68	0.917	2.54	– 12.03 ± 0.84 [d]
18.67	1.09	80.24	2.20	0.0255	7.12	0.923	2.35	– 11.88 ± 0.77 [d]
14.57	1.34	84.09	1.63	0.0299	5.53	0.942	1.70	– 11.53 ± 0.57 [d]
10.88	1.64	87.48	1.17	0.0352	4.26	0.958	0.99	– 11.33 ± 0.41
8.59	2.05	89.36	0.91	0.0431	3.63	0.968	0.53	– 11.25 ± 0.32
7.60	2.20	90.20	0.79	0.0458	3.35	0.971	0.29	– 11.25 ± 0.28

a: Solid Na_2CO_3 present (saturated solution).

b: $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ completely dissolved.

c: The large uncertainties arise from the ionic strength corrections (error propagation accounting for the uncertainties of the SIT coefficients)

d: At $I > 5$ mol·kg^{-1}, which is outside the validity range of the SIT, the calculated $\log_{10} K^{\circ}_{s,5}$ values show a systematic increase. They are not considered in the mean value accepted by this review.

For the calculation of the solubility constant and ionic strength, the increase of the Na^+ concentration and ionic strength caused by the dissolution of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ is taken into account. The mean value from data at $I <$ 5 mol·kg^{-1}, $\log_{10} K^{\circ}_{s,5} = -(11.3 \pm 0.3)$, is used together with similar values derived from the study of [1973DER/FAU3] to select thermodynamic data for this solid phase.

[1961VIC/DOU2]

The enthalpy of thorium dioxide relative to 273.15 K was measured at ten temperatures from 323 to 1173 K. A Bunsen ice drop calorimeter was used to make the measurements on two samples of widely different bulk densities. The corresponding heat-capacity values for the higher density sample are represented within their uncertainty (estimated to be ± 0.3 to 0.5%) by the following equation:

$$C^{\circ}_{p,\mathrm{m}}(T) = 71.366 + 7.556 \times 10^{-3}\,T - 10.529 \times 10^{5}\,T^{-2} \quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

At 298.15 K this equation agrees well with previously reported low-temperature measurements made with an adiabatic calorimeter [1953OSB/WES]. Values of heat content, heat capacity, entropy, and Gibbs energy function are tabulated from 298.15 to 1200 K. These data were included in the data fitting.

[1962FAU/DER]

The constitution of the limiting complex in the Th(IV)-carbonate system has been determined using potentiometric titrations (measuring the free hydrogen ion concentration at different carbonate concentrations). The experiments have been made in a KNO_3 ionic medium, and the authors have only determined the equivalence point where the limiting complex is formed, but no equilibrium constants. The authors have tested different models and their titration curves are only consistent with the stoichiometry $Th(CO_3)_5^{6-}$; the compositions $Th(CO_3)_4^{4-}$, $Th(CO_3)_6^{8-}$ and $Th(CO_3)_4(OH)_2^{6-}$ were ruled out. There are few experimental details in this short communication and the experimental data can therefore not be reinterpreted by this review. However, the study seems well done and the suggested stoichiometry is considered reliable by this review.

[1962FAU/DER2]

The constitution of the thorium(IV) carbonate complex formed at high carbonate concentration has been determined by cryoscopy. This is a method that provides information about the number of solute particles in solution and for the case of complex formation reactions, the change in this number as a result of complex formation, *e.g.* for the reaction $Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}$ there is a decrease of five. The authors have determined the molar freezing point depression and this is used to test the stoichiometry of the complexes formed. One important conclusion from this study is that the experimental data are only consistent with the stoichiometry $Th(CO_3)_5^{6-}$. Experimental data of this type cannot be made in a medium of constant ionic strength and it is also not possible to determine equilibrium constants. However, the proposed stoichiometry is in agreement with that proposed in a large number of other studies.

[1962KAR/VOL]

The authors have used IR spectroscopy and suggested that the compound $Na_6[Th(CO_3)_5]\cdot 12H_2O$ is a double-salt with the composition $Na_4[Th(CO_3)_4]\cdot Na_2CO_3\cdot 12H_2O$; X-ray structure data [1975VOL/RIM2], [1975VOL/RIM3] clearly demonstrate that this conclusion is in error and this review does not consider the use of qualitative IR data for structure and bonding assignments as reliable. There are no thermodynamic data in this study.

[1962NIK/LUK]

The solubility of thorium tetrafluoride was investigated as a function of $HClO_4$ molarity. The solid was precipitated by reacting thorium nitrate with hydrofluoric acid. The solid was suspended in test solutions with five fixed concentrations of $HClO_4$ ranging from 0.1 to 1.1 M at 25°C. The suspensions were stirred for 12 hours. Filtered solutions (unspecified pore size) were analysed for thorium gravimetrically by precipitation of the hydroxide and weighing as ThO_2. The authors report solubility in terms of ThF_4 ($g\cdot L^{-1}$) as a function of the $HClO_4$ concentrations. They also report the pH values for these samples. From these data they calculated the solubility product for the solid and the value of the equilibrium constant for ThF^{3+}. The values they report are based on data obtained in this study and the values of fluoride and hydroxide complexes of thorium from the literature, which in turn are based on different chemical systems and different ionic strengths.

This study was not conducted at a fixed ionic strength, so evidence for the equilibrium with the solid phase is lacking. As the reported values for the solubility product of ThF_4(cr, hyd) vary by 1.5 orders of magnitude, and values of thorium fluoride and hydrolysis constants from different chemical systems and ionic strengths were combined, this review does not consider the calculated solubility product (4.5×10^{-26} $(\text{mol·L}^{-1})^5$) to be reliable.

[1962PEP/NAM]

This is a detailed study of the extraction equilibria in the toluene-Th(IV)-hydrogen 2-ethylhexyl phosphonate-Cl^-- NO_3^- systems. There is no quantitative information on the formation of complexes between thorium and Cl^- or NO_3^- in the aqueous phase, only a qualitative statement that $Th(NO_3)^{3+}$ and $Th(NO_3)_2^{2+}$ complexes are extracted to a much greater extent than the corresponding chloride complexes.

[1962PET/REX]

This paper mainly concerns the diffusion of hydrogen in the ThH_{2-x}(cr) phase, but the composition of this phase was also determined as a function of temperature and pressure of hydrogen from 773 to 1073 K. Crystal bar thorium, whose principal impurities were 0.145 wt% C and 0.19 wt% O was used. By using these data the diffusion coefficients of hydrogen in ThH_{2-x}(cr) were calculated from previous measurements of the parabolic reaction rate constants. Although no values for the equilibrium pressures in the {Th(cr) + ThH_{2-x}} region were quoted by the authors, Flotow *et al.* [1984FLO/HAS] have derived these values from the paper, and these are discussed in Section VII.2.1.2.2.

[1962PRA/DEY]

Prasad and Dey [1962PRA/DEY] performed potentiometric titrations of 0.005 to 0.05 M $ThCl_4$ solutions with NaOH solutions of different concentrations from pH 3 to pH 11 − 12 and reverse titrations by adding 0.04 and 0.08 M $ThCl_4$ to the NaOH test solutions at 27°C. Ionic strength was not kept constant and the calibration of the glass-calomel electrode system used to measure pH is not mentioned. The authors report only the qualitative results that precipitation occurs already at $\bar{n}_{OH} < 4$ (which is concluded from the inflection points of the titration curves) and that precipitation is complete near pH 7, independent of the thorium concentration. No thermodynamic data can be derived from this study.

[1963ACK/RAU]

The evaporation behaviour of the Th-O system was studied at *ca.* 2200 to 2900 K. The results of the effusion measurements of the dioxide phase and {liquid metal + dioxide} mixtures and a mass spectrometric investigation of the former were combined to yield an internally consistent set of thermodynamic data for the system.

The thorium used was of 99% purity, as established by spectroscopic analysis. The mass effusion rate from ThO_2(cr) contained in a tungsten effusion cell was measured from 2180 to 2871 K, both by collection, plus activation analysis, and, over a much smaller temperature range, by using a vacuum thermobalance. The results agreed excellently.

The solid dioxide evaporates congruently at all temperatures. Above 2800 K, the thoria in equilibrium with Th(l) showed a measurable but thermodynamically insignificant hypostoichiometry to a composition of $ThO_{1.998}$. The "effective" pressure, (*i.e.* the pressure assuming the vapour is composed entirely of ThO_2) is given by the equation $\log_{10} p_{\mathrm{e}} / \mathrm{bar} = -35500/T + 8.265$.

A mass-spectrometric study of the vaporisation from ThO_2(cr) from tungsten cells at temperatures from *ca.* 2500 to 2825 K showed that the vapour in fact contains similar amounts of ThO(g) and ThO_2(g).

In a limited study of the pressure of ThO(g) from Th(l) + ThO_2 mixtures, there were problems with movement of Th(l) out of or through the containing ThO_2 cup due to dissolution of ThO_2 in the melt, but reasonable success was achieved for the initial period of the runs.

These data were used to calculate the Gibbs energies of formation of ThO(g) and ThO_2(g), which are not quoted here, since there are now better data for the thermal functions of many of the substances concerned – see Sections VII.1.1.2 and VII.1.3.2. The data in this publication were also re-evaluated by [1973ACK/RAU2], using better defined values for $\Delta_{\mathrm{f}} G_{\mathrm{m}}$ (ThO, g).

The reaction occurring in thoriated tungsten filaments was also discussed.

[1963ALL/MCD]

The authors have used a liquid ion exchanger, di-*n*-decylamine sulphate to determine the stepwise equilibrium constants at 25°C for the reactions:

$$\mathrm{Th(SO_4)_2(aq)} + \mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Th(SO_4)_3^{2-}} \tag{A.41}$$

$$\mathrm{Th(SO_4)_2(aq)} + 2\mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Th(SO_4)_4^{4-}} \tag{A.42}$$

The experiments have been made by varying the total concentrations of Th(IV) from 6.00×10^{-6} to 64.8×10^{-6} M in a mixed H_2SO_4-Na_2SO_4 medium with varying ionic strength. The acidity is sufficiently high to avoid significant hydrolysis of thorium. The composition of the organic phase has been kept very nearly constant in the different test solutions, ensuring that the activity of the extracted uncharged complex $Th(SO_4)_2$ is constant; as the two phases are in equilibrium the activity of this species in the aqueous phase is also constant. The experiments are made in such a way that $[Th(SO_4)_2]_{org}$ is kept constant by varying the total concentrations of thorium and sulphate. The equilibrium constants for Equations (A.41) and (A.42), $K_{2,3}$ and $K_{2,4}$ respectively, were calculated by using the mass balance equation:

$$Th_{tot} = [Th(SO_4)_2] + [Th(SO_4)_2][SO_4^{2-}]K_{2,3}G_{3,2} + [Th(SO_4)_2][SO_4^{2-}]^2K_{2,4}G_{4,2} \quad (A.43)$$

$G_{3,2}$ and $G_{4,2}$ are activity correction factors calculated by using the Debye-Hückel term for the reactions and assuming this to be equal to unity for the uncharged complex. The total concentration of thorium is so low that it does not have any significant effect on the mass balance for sulphate. Allen and McDowell report $K_{2,3}$ (A.41) = (5.7 ± 1.2) and $K_{2,4}$(A.42) = (0.054 ± 0.009), where the errors are at the 95% confidence limit and refer to zero ionic strength.

The changes in the composition of the aqueous phase in these experiments are very large from 0.094 M H_2SO_4/0.006 M Na_2SO_4 to 0.190 M H_2SO_4/1.30 M Na_2SO_4 and there is no reason to assume that the simple Debye-Hückel term will provide an accurate description the variation in the activity coefficients of sulphate and the negatively charged Th(IV) complexes. The experimental data in [1963ALL/MCD] therefore need to be reinterpreted.

The NONLINT-SIT code (Appendix D) was used for this, with $\Delta_f G_m^o / RT$ values of $-(598.638 \pm 0.737)$ for $ThSO_4^{2+}$ and of $-(906.869 \pm 0.622)$ for $Th(SO_4)_2(aq)$, selected in this review. These values are based on several other sources and ion interaction parameters $\varepsilon(Na^+, SO_4^{2-})$ and $\varepsilon(Na^+, HSO_4^-)$ from [2003GUI/FAN], and making the reasonable assumptions that the ion interaction parameters $\varepsilon(H^+, Th(SO_4)_3^{2-})$ and $\varepsilon(H^+, HSO_4^-)$ are approximately equal, respectively to $\varepsilon(Li^+, SO_4^{2-})$ and $\varepsilon(H^+, ClO_4^-)$ (as reported by [2003GUI/FAN]). The values of $\Delta_f G_m^o / RT$ for $Th(SO_4)_3^{2-}$ and $\varepsilon(Na^+, Th(SO_4)_3^{2-})$ were fitted simultaneously using the known equilibrium constants for the formation of $Th(SO_4)^{2+}$ and $Th(SO_4)_2(aq)$ and the interaction coefficients mentioned above (for details see Section IX.1.3.2). These analyses provided a $\Delta_f G_m^o / RT$ value of $-(1209.432 \pm 0.086)$ for $Th(SO_4)_3^{2-}$ and $\log_{10} \beta_3^o = (10.748 \pm 0.076)$, and $\varepsilon_1(Na^+, Th(SO_4)_3^{2-}) = (0.091 \pm 0.038)$ kg·mol^{-1}, which were selected in this review. Predicted concentrations, using the aqueous phase model selected in this review, are compared against the experimental data in Figure IX-2 (see Section IX.1.3.2) and the details are provided in Table A-23. A close agreement is observed between the predicted and experimentally observed Th concentrations. These comparisons (Figure IX-2) show that $Th(SO_4)_3^{2-}$ is the dominant species in this experiment and this species was selected for calculations involving solubilities of different Th-sulphate solids (Section IX.1.3.3) where this species is dominant and is needed for interpretation of solubility data.

Table A-23: Observed [1963ALL/MCD] and predicted aqueous thorium concentrations at 25°C for solvent extraction studies in Na_2SO_4 (data are plotted in Figure IX-2).

Experimental concentrations (m)			Predicted concentrations (m)				
Na^+ total	SO_4^{2-} total	Th total $\times10^5$	Th total $\times10^5$	Th^{4+} $\times10^5$	$ThSO_4^{2+}$ $\times10^5$	$Th(SO_4)_2(aq)$ $\times10^5$	$Th(SO_4)_3^{2-}$ $\times10^5$
1.210×10^{-2}	1.010×10^{-1}	6.003×10^{-1}	6.479×10^{-1}	1.497×10^{-4}	5.971×10^{-2}	4.619×10^{-1}	1.261×10^{-1}
3.620×10^{-2}	1.170×10^{-1}	6.363×10^{-1}	6.732×10^{-1}	1.389×10^{-4}	5.453×10^{-2}	4.619×10^{-1}	1.566×10^{-1}
8.040×10^{-2}	1.420×10^{-1}	7.393×10^{-1}	7.230×10^{-1}	1.282×10^{-4}	4.836×10^{-2}	4.619×10^{-1}	2.126×10^{-1}
1.710×10^{-1}	1.920×10^{-1}	8.793×10^{-1}	8.469×10^{-1}	1.181×10^{-4}	4.073×10^{-2}	4.619×10^{-1}	3.442×10^{-1}
1.910×10^{-1}	2.020×10^{-1}	9.523×10^{-1}	8.778×10^{-1}	1.164×10^{-4}	3.945×10^{-2}	4.619×10^{-1}	3.763×10^{-1}
2.620×10^{-1}	2.430×10^{-1}	1.060	9.915×10^{-1}	1.163×10^{-4}	3.650×10^{-2}	4.619×10^{-1}	4.930×10^{-1}
3.730×10^{-1}	3.040×10^{-1}	1.210	1.185	1.177×10^{-4}	3.329×10^{-2}	4.619×10^{-1}	6.899×10^{-1}
7.290×10^{-1}	4.970×10^{-1}	1.830	1.843	1.328×10^{-4}	2.897×10^{-2}	4.619×10^{-1}	1.352
9.430×10^{-1}	6.110×10^{-1}	2.160	2.265	1.413×10^{-4}	2.766×10^{-2}	4.619×10^{-1}	1.775
1.137	7.140×10^{-1}	2.620	2.651	1.485×10^{-4}	2.689×10^{-2}	4.619×10^{-1}	2.162
1.333	8.200×10^{-1}	2.930	3.056	1.541×10^{-4}	2.628×10^{-2}	4.619×10^{-1}	2.568
1.725	1.028	3.780	3.913	1.624×10^{-4}	2.532×10^{-2}	4.619×10^{-1}	3.426
1.924	1.134	4.320	4.379	1.649×10^{-4}	2.490×10^{-2}	4.619×10^{-1}	3.892
2.124	1.241	4.800	4.873	1.662×10^{-4}	2.450×10^{-2}	4.619×10^{-1}	4.386
2.324	1.351	5.450	5.388	1.659×10^{-4}	2.415×10^{-2}	4.619×10^{-1}	4.902
2.520	1.455	6.060	5.925	1.656×10^{-4}	2.380×10^{-2}	4.619×10^{-1}	5.439
2.720	1.561	6.780	6.511	1.647×10^{-4}	2.343×10^{-2}	4.619×10^{-1}	6.026

[1963BIL/FUR]

Bilinski *et al.* [1963BIL/FUR] report the titration of thorium nitrate solutions ($[Th]_{tot} = 3\times10^{-5}$ to 0.1 M) with KOH solutions of varying concentrations at (20 ± 0.1)°C. The onset of precipitation was measured by a tyndallometric (light scattering) method as a function of the total metal concentration and pH. The lower limit for the detection of precipitation was at $[Th]_{tot} = 3\times10^{-5}$ M. A glass electrode was used for pH measurements; however, neither its calibration nor the pK_w values or activity coefficients used to convert the measured pH values into $\log_{10}[OH^-]$ are mentioned.

The solubility curve of thorium hydroxide shown in Figure 5 in [1963BIL/FUR], where $\log_{10}[Th]_{tot}$ is plotted against pH measured after 24 hours in the thorium hydroxide suspensions, is evaluated by slope analysis and described by the following reactions and equilibrium constants:

pH 3.1 to 3.4: $Th(OH)_4(s) \rightleftharpoons Th^{4+} + 4OH^-$ $\quad \log_{10} K_{s,0} = -(45.7 \pm 0.2)$

pH 3.5 to 4.1: $Th(OH)_4(s) \rightleftharpoons (1/n)\,((Th(OH)_2^{2+})_n + 2OH^-$ $\quad \log_{10} K_{s,2} = -(24.3 \pm 0.2)$

The possible formation of $Th(OH)^{3+}$ and other polynuclear species than (4,2) and (8,4) was neglected. The authors also neglected the fact that the activity coefficients depend strongly on the initial thorium nitrate concentration since no background electrolyte was added to maintain the ionic strength constant. The variation of ionic strength along the solubility curve does not allow the simple slope analysis to be used. A cumulative hydrolysis constant of $^{*}\beta_2 = 1.029 \times 10^{-7}$ ($\log_{10} {}^{*}\beta_2 = -6.99$) is given in the abstract of [1963BIL/FUR]. The calculation of this value, which is not consistent with the difference between $\log_{10} K_{s,2}$ and $\log_{10} K_{s,0}$, is not explained. For these reasons the equilibrium constants calculated in [1963BIL/FUR] are not accepted by this review.

Additional titration experiments in the presence of $10^{-5} - 10^{-2}$ M carbonate at $[Th]_{tot} = 4 \times 10^{-4}$ M led to a decrease of the turbidity at pH 9 − 10.4, partly even to clear solutions, due to the formation of thorium complexes with carbonate. However, these results do not allow a quantitative interpretation.

[1963GIN/EFI]

Gingerich and Efimenko have measured mass-spectrometrically the pressures of the elemental phosphorus species over thorium phosphides from $ThP_{0.63}$ to $ThP_{1.27}$ from 1131 to 2243 K. The authors indicate that their measured phosphorus pressures are too low, at least for the higher phosphide compositions, owing to slow diffusion in the surface layers. A further reason for suspecting these data is that, as noted by [1975RAN], above 1900 K, the equilibrium constants for the reaction $P_2(g) \rightleftharpoons 2P(g)$ are 4 to 9 times greater than those calculated from the assessed data by the Gurvich *et al.* [1989GUR/VEY] and much greater at lower temperatures. The three measurements of the $P_4(g)$ pressures (from 1416 to 1482 K) are even further from equilibrium. These factors suggest that equilibrium was not attained in this study, even at the highest temperatures, and the data from this study have not been used by the review.

[1963LIN]

In this quite detailed Progress Report, Linevsky reports the results of IR spectra of ThO_2 molecules condensed in a solid argon matrix, using both normal ThO_2 and a sample enriched in ^{18}O (*ca.* 45%). By a comparison of the observed peaks, the symmetric and anti-symmetric stretch frequencies for $Th^{16}O_2$ were identified at $\upsilon_1 = 786.8$ cm^{-1} and $\upsilon_3 = 734.5$ cm^{-1} respectively. From the corresponding frequencies for $Th^{18}O_2$, 743.8 cm^{-1} and 659.9 cm^{-1}, the O-Th-O apex angle was estimated to be 106°, with an unspecified, but large, uncertainty (due to the large mass ratio of the Th and O atoms). Doublets due to the ThO(g) molecule were also observed. Linevsky further suggests that the υ_2 bending frequency is below the lower limit of their instrumentation, 180 cm^{-1}, since no peaks were observed in this region.

[1962MAT/MIL]

The paper provides information on precipitation curves of colloids when K_2HPO_4 solutions is added to solutions of Th(IV) nitrate. This study provides no thermodynamic information.

[1963RYA/VOL]

The paper contains a brief review of older studies of thorium carbonate systems, a high-frequency titration study to establish the stoichiometry of the limiting complex and finally the preparation and characterisation of some solid carbonate phases. The high-frequency titration is the part of main interest for this review. The experiment consists of a titration where the current through a titration cell is measured as a function of the ratio between the total concentrations of Th(IV) and carbonate. The titration curves display sudden changes in slope at different ratios Th(IV)/carbonate and this is used as an indicator for the stoichiometry of the complexes formed. In the present case the titration curve when ammonium carbonate is titrated with thorium nitrate, is linear at low values of the ratio and bends at a ratio 1:4. The curve is then linear until a ratio slightly larger than 1:2. In the reverse titration there is a sharp bend in the curve at a ratio Th(IV)/carbonate = 2, but only a gradual change of the slope at higher values. There is no justification why the curve should display a sudden change in slope at a certain ratio; on the contrary in stepwise complex formation reactions one would in general expect a gradual change of properties. For this reason the present review does not accept the stoichiometry proposed by Ryabchikov *et al.* The characterisation of the solid phases has been made by X-ray powder diffraction and thermogravimetry and the authors conclude, based on these data, that the solid phase $M_6[Th(CO_3)_5]\cdot12H_2O$; M = Na, K, is the double salt $M_4[Th(CO_3)_4]\cdot M_2CO_3.12H_2O$; this conclusion is erroneous as shown by the known single crystal structure of the compound with M = Na, [1975VOL/RIM3], [1975VOL/RIM4].

[1963VOR/DAN]

The authors report the rates of evaporation of ThO_2(cr) at *ca.* 1803, 2023 and 2233 K, (the data are only reported graphically) but do not convert these to vapour pressures, unlike their similar study on UO_2(cr) in the same paper. If the data for ThO_2 are converted to pressures using the Langmuir equation, the ratio of the experimental pressures to those calculated from the final assessed data are respectively 38, 5.6 and 0.19, a variability reflected in the very large uncertainty of the derived third-law enthalpy of sublimation quoted in Section VII.1.2.2. These data have been included in the weighted average, but with that very large uncertainty.

[1963WIS/EGA]

This is a study of the thermodynamic properties of solutions of the actinides and some fission products in liquid bismuth. For dissolution of thorium, the cell

$$\mathrm{Th(cr)} \mid \mathrm{LiCl\text{-}KCl\ (eutectic)} + 5\%\ \mathrm{ThCl_4} \mid \mathrm{Bi\text{-}Th(l)}$$

was used. Values of the emf are quoted for 1073 K only, the mole fraction of thorium in the Th-Bi melt varying from 0.00135 to 0.0080 (six different values). The derived values of the thorium potential in this range correspond to an excess Gibbs energy of solution of thorium of $-(118.0 \pm 0.8)$ kJ·mol^{-1}, the uncertainty showing the range of values only.

[1963YEN/LI]

For this study of the properties of $ThOCl_2$(cr), ThO_2 was obtained by heating to 873 K a thorium oxalate precipitated from a thorium nitrate solution. $ThCl_4$(cr) was prepared by chlorinating ThO_2 at 873 to 923 K with a "mixture of S_2Cl_2 (SCl_2) vapour and Cl_2". $ThOCl_2$(cr) was obtained by direct reaction of ThO_2 and $ThCl_4$. Analyses yielded the compositions $ThCl_{3.98\pm0.02}$ and $ThOCl_{1.98\pm0.03}$.

The phase diagram of the ThO_2-$ThCl_4$ system was investigated in order to prove the existence of $ThOCl_2$(cr) and to demonstrate that the compound could be obtained from the reaction of ThO_2 with $ThCl_4$. The melting point of $ThCl_4$ was 1040−1043 K for different batches, in agreement with earlier data. A eutectic at 988 K was observed from 50 to 100 mol% $ThCl_4$, presumed to be between $ThOCl_2$(cr) and $ThCl_4$(cr) but the details of the other parts of the diagram are not clear.

The enthalpy of formation of $ThOCl_2$(cr) at 298.15 K was obtained from the comparison of the enthalpies of solution of $ThCl_4$(cr) and $ThOCl_2$(cr) in 0.1 M NaOH, under the same conditions, in order to eliminate the uncertainties associated with the formation of the thorium hydroxide precipitate.

The experimental reactions were:

$$\mathrm{ThOCl_2(cr)} + \{\mathrm{2NaOH{+}H_2O}\}\ (\text{in NaOH}\cdot550\,\mathrm{H_2O}) \rightleftharpoons \{\mathrm{Th(OH)_4(ppt)} + \mathrm{2NaCl}\}\ (\text{in NaOH}\cdot550\,\mathrm{H_2O}) \qquad (A.44)$$

$$\mathrm{ThCl_4(cr)} + 4\ \mathrm{NaOH}\ (\text{in NaOH}\cdot550\,\mathrm{H_2O}) \rightleftharpoons \{\mathrm{Th(OH)_4(ppt)} + \mathrm{4NaCl}\}\ (\text{in NaOH}\cdot550\,\mathrm{H_2O}) \qquad (A.45)$$

$$\Delta_r H^\circ_m\,(A.44) = -(129.33 \pm 1.38)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_r H^\circ_m\,(A.45) = -(336.64 \pm 2.03)\ \mathrm{kJ\cdot mol^{-1}}.$$

The authors also measured the vapour pressure of $ThCl_4$(g) at four temperatures from 953 to 1025 K by the modified boiling point method, and, more extensively, the pressure of $ThCl_4$(g) in the decomposition reaction $2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$ from 1040 to 1182 K. For the latter, the pressures were given by

$\log_{10} p_{\mathrm{ThCl_4}}/\mathrm{bar} = -(72500/4.575\,T) + 12.64$. The results were processed by the review by the second-law to give the enthalpy of formation and standard entropy of the oxychloride.

All these results are used, in conjunction with other studies, in the evaluation of the enthalpy of formation of $ThOCl_2$(cr) in Section VIII.2.1.6.

[1964ARO]

Thermodynamic data in the Th–C system were obtained from measurements on solid electrochemical cells of the following types, at 1073 to 1273 K:

$$\mathrm{Th + ThF_4 \mid CaF_2 \mid ThF_4 + \text{“}ThC_2\text{”} + C}$$

$$\mathrm{Th + ThF_4 \mid CaF_2 \mid ThF_4 + \text{“}ThC_2\text{”} + \text{“}ThC\text{”}}$$

$$\mathrm{Th + ThF_4 \mid CaF_2 \mid ThF_4 + ThC_{1-x} + Th}$$

from which the chemical potentials in the relevant diphasic fields can be determined. Further processing of these data is complicated by the varying and ill-defined phase boundaries of the carbide phases, but the derived data for the Gibbs energies of ThC_{2-x} are discussed in Section XI.1.1.4.

[1964CAT/THO]

The authors attempted to measure the vaporisation of ThS from by effusion from a tantalum cell 1935 to 2464 K, but found that the measured “pressures” were unreasonably high, due to “flow” of ThS over the surface of the container, despite the temperatures being well below the melting point of ThS(cr) (> 2600 K), and give an estimated equation for the effective pressure, based on the measured slope of their (incorrect) measurements and an estimated entropy of vaporisation. These data have been processed in a somewhat different way in Section IX.1.1.3, following the analysis of Rand [1975RAN], as corrected by [1984GRO/DRO].

[1964EGA]

The Gibbs energy of formation of “ThC_2” at 973 to 1243 K was determined using a solid-state emf cell Th,ThF_4(s)|CaF_2(s)|ThF_4, “ThC_2”,C with molybdenum electrodes. The dicarbide + graphite +ThF_4 mixture was prepared by heating Th + excess graphite, heating to 1923 K for 30 min, crushing, admixing ThF_4(cr) and repelleting. Four to seven days were required for equilibrium to be attained.

[1964HIE/SIL]

This preliminary paper of Hietanen and Sillén on the hydrolysis of Th(IV) in 3 M (Na)Cl medium is discussed together with a later paper of these authors [1968HIE/SIL] where the results of both studies are evaluated and discussed more detailed.

[1964HOL/GRE]

Torsion effusion measurements were made of the pressures of CO(g) in the reaction of ThO_2 and graphite $ThO_2 + 2C(cr) \rightleftharpoons$ "ThC_2" + 2CO(g) from *ca.* 1560 to 1680 K. Samples of ThO_2(cr) were held in graphite effusion cells heated in a molybdenum furnace. Measurements of the vapour pressure of zinc were used to calibrate the torsion wire, rather than an absolute determination. The measured pressures varied slightly with orifice area, but when extrapolated to zero orifice size were given by the equation: $\log_{10} p_{CO} / \text{bar} = -21830\,T^{-1} + 8.45$ in the range 1560 to 1680 K. These results are included in the comparison of similar studies in Section XI.1.1.4.

[1964JAC/BAR]

A mass spectrometric investigation of the vaporisation processes of solid ThC_2(s), contained in a graphite Knudsen cell is reported. 'ThC_2'(cr) was prepared from the elements by arc-melting, and characterised by X-ray diffraction immediately after preparation. The initial thorium contained *ca.* 1% ThO_2, but the oxygen was presumably removed during arc melting, since no ThO(g) was found in the mass-spectrometric studies. Ion intensities were converted to partial pressures by calibration with both silver and molybdenum.

The partial pressures of Th(g) and ThC_2(g) in equilibrium with the carbon-saturated solid were of comparable magnitude in the temperature range investigated, 2371 − 2642 K. The authors do not, curiously, give pressures of both Th(g) and ThC_2(g) at the same temperature. Instead, they report individual pressures of ThC_2(g) at one set of temperatures (2371 − 2641 K) for the reaction:

$$ThC_2(\text{cr, carbon saturated}) \rightleftharpoons ThC_2(g) \qquad (A.46)$$

and pressures of Th(g) in the reaction

$$ThC_2(\text{cr, carbon saturated}) \rightleftharpoons Th(g) + 2C(cr) \qquad (A.47)$$

at a different set of temperatures (2411 − 2642 K).

The data were analysed by the authors by both second- and third-law methods, using estimated thermal functions for both ThC_2(cr) and ThC_2(g), with reasonable agreement for both the above reactions. However, as noted in Sections XI.1.1 and XI.1.2, most of the thermodynamic data for both these species are uncertain. The authors assumed that the ThC_2(g) molecule had the linear C=Th=C structure, and the electronic contribution to the partition function for ThC_2(g) was based on that for the Th^{2+}(g) ion. Both of these assumptions are now almost certainly incorrect, see below.

The uncertainty from the data for ThC_2(cr) can be removed by subtracting the fitted linear Gibbs energies for the Reactions (A.46) and (A.47) above, to give that for the reaction:

$$\mathrm{ThC_2(g)} \rightarrow \mathrm{Th(g)} + 2\mathrm{C(cr)} \qquad \text{(A.48)}$$

$$[\Delta_r G^o_m]^{2560\,\mathrm{K}}_{2350\,\mathrm{K}}((\mathrm{A.48}), T) = 67632 - 29.325\,T \quad \mathrm{J\cdot mol^{-1}}$$

As discussed in Section (XI.1.2.1), recent calculations by Kovács and Konings [2008KOV/KON] suggest that $ThC_2(g)$ is not linear, but has an asymmetric L-shaped structure. With the thermal functions and vibration frequencies calculated from this structure, and an electronic contribution to the partition function based on that for ThO(g), the third law enthalpy of formation of $ThC_2(g)$ from the data of [1964JAC/BAR] is calculated to be $\Delta_f H^o_m$ (ThC_2, g, 298.15 K) = (784.7 ± 9.2) $\mathrm{kJ\cdot mol^{-1}}$, where the uncertainty does not include those from the experimental difficulties (conversion from ion intensities to pressures, *etc.*) and in the estimated electronic contribution for $ThC_2(g)$.

Moreover, the experimental and calculated entropies of Reaction (A.48) at 2500 K are distinctly different (29.3 *vs.* 61.6 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$). In view of these inconsistencies, no data are selected for $ThC_2(g)$ for this review.

[1964NAB/KUD]

Nabivanets and Kudritskaya studied the solubility of an amorphous $Th(OH)_4(am)$ precipitate in 0.1 M $NaClO_4$ at (17 ± 1)°C. The solubility was measured in the pH range 3.4 to 7.0 after equilibration times of 3 − 6 days. The Th concentrations were determined colorimetrically after centrifugation for 1 hour at 10000 rpm with a usual laboratory centrifuge. The measured solubilities, which decrease from 1.6×10^{-3} M at pH 3.40 to 5×10^{-7} M at pH 5.35 − 7.00, were described by assuming only the presence of mononuclear Th(IV) hydroxide complexes. The stepwise equilibrium constants for the reactions:

$$\mathrm{Th(OH)}^{4-n+1}_{n-1} + \mathrm{OH^-} \rightleftharpoons \mathrm{Th(OH)}^{4-n}_{n},$$

were calculated by slope analysis. The following final results, *i.e.*, the solubility product $\log_{10} K_{s,0}$ for the reaction:

$$\mathrm{Th(OH)_4(am)} \rightleftharpoons \mathrm{Th^{4+}} + 4\mathrm{OH^-} \qquad \text{(A.49)}$$

and the formation constants $\log_{10} \beta_n(\mathrm{Th(OH)}^{4-n}_n)$ for the reactions

$$\mathrm{Th^{4+}} + n\mathrm{OH^-} \rightleftharpoons \mathrm{Th(OH)}^{4-n}_n \qquad \text{(A.50)}$$

were reported in [1964NAB/KUD]:

$$\log_{10} K_{s,0}\,(\mathrm{A.49}) = -41.14$$

$$\log_{10} \beta_1\,(\mathrm{A.50}), n = 1) = (9.40 \pm 0.24)$$

$$\log_{10} \beta_2\,(\mathrm{A.50}), n = 2) = (18.25 \pm 0.37)$$

$$\log_{10} \beta_3\,(\mathrm{A.50}), n = 3) = (26.74 \pm 0.41)$$

$$\log_{10} \beta_4\,(\mathrm{A.50}), n = 4) = (34.82 \pm 0.44).$$

The solubility data at pH < 5.4 are consistent with corresponding data reported in other solubility studies with $Th(OH)_4(am)$ or $ThO_2(am, hyd)$. However, the constant, pH-independent Th concentration of $\log_{10}[Th] = -(6.30 \pm 0.02)$ measured at pH 5.4 to 7.0 is more than two orders of magnitude higher than corresponding data obtained after 1−2 nm ultrafiltration or ultracentrifugation [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2000RAI/MOO], [2002NEC/MUL]. Neck *et al.* have shown that the centrifugal force used in the study of Nabivanets and Kudritskaya [1964NAB/KUD] is not sufficient to remove small Th(IV) colloids; this requires ultracentrifugation, *e.g.*, at 90000 rpm corresponding to 5×10^5 g [2002NEC/MUL], [2004ALT/NEC]. It is noteworthy that Th concentrations in neutral and alkaline solutions were found to be exactly the same ($\log_{10}[Th] = -(6.3 \pm 0.5)$ [2004ALT/NEC]) when aliquots were taken from the supernatant solution without filtration or centrifugation. They must be ascribed to colloidal or polynuclear species $(4m,m) = Th_m(OH)_{4m}(aq)$.

As ultracentrifugation and potentiometric studies have shown that polynuclear species are predominant at the thorium concentrations and pH values in the saturated solutions of [1964NAB/KUD], the reported equilibrium constants for mononuclear hydroxide complexes have no chemical significance. Using the hydrolysis constants and ion interaction coefficients selected in the present review, the solubility data of Nabivanets and Kudritskaya at pH 3.5−4.5 have been reinterpreted (Figure A-12). The complex $Th_4(OH)_{12}^{4+}$ is found to be predominant along the solubility curve. The solubility constants recalculated from the data in 0.1 M $NaClO_4$,

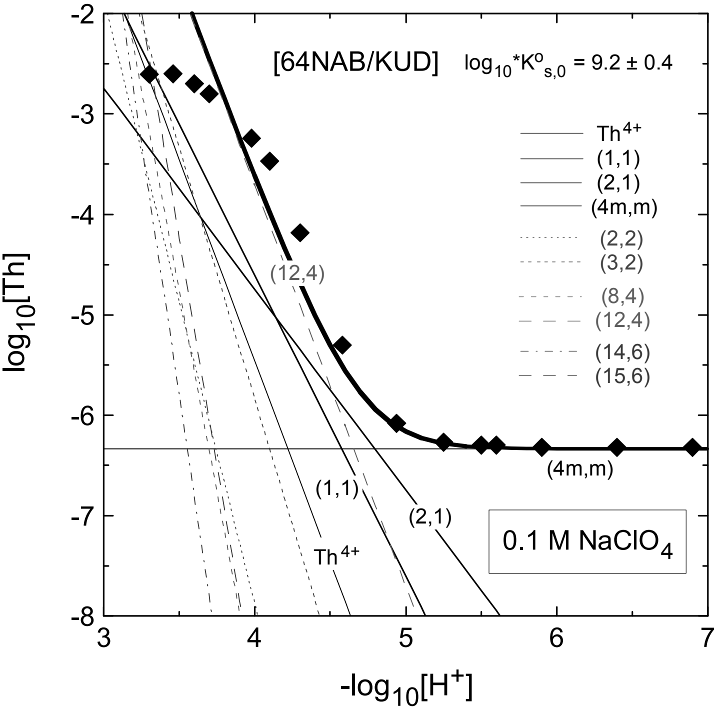
$$\log_{10} {}^{*}K_{s,0} = (10.5 \pm 0.4)\ (\log_{10} K_{s,0} = -(44.7 \pm 0.4)),$$

correspond to following equilibrium constants at zero ionic strength:

$$\log_{10} {}^{*}K^{\circ}_{s,0} = (9.2 \pm 0.4)\ (\log_{10} K^{\circ}_{s,0} = -(46.8 \pm 0.4)).$$

Because of the large scatter of solubility data for amorphous Th(IV) precipitates, this review did not carry out temperature corrections for the hydrolysis constants used and the solubility constant calculated from the data at 17°C [1964NAB/KUD] are compared to the standard state temperature of 298.15 K (25°C).

Figure A-12: Solubility of thorium hydroxide determined by Nabivanets and Kudritskaya [1964NAB/KUD] at 17°C in 0.1 M $NaClO_4$. The calculated lines are based on the hydrolysis constants and ion interaction coefficients selected in this review, $\log_{10} {}^*K^{\circ}_{s,0} = 9.2$, and $\log_{10} K_{s,(4m,m)} = -6.3$.



[1964NAB/KUD2]

Only a document in Russian was available to the reviewers and only a few comments can therefore be made on this paper. The electrodialysis experiments seem to give, at best, qualitative information on the speciation and will not be further discussed. The ion-exchange experiments have been made using the Fronaeus method where the distribution of thorium between an aqueous solution and a cation exchanger is measured as a function of the ligand concentration. When analysing the data, the distribution coefficient of both Th^{4+} and the positively charged complexes are taken into account. The experiments have been made at an ionic strength of 4 M in a medium of the composition: (4.00 − L) M $HClO_4$ and L M HCl or HNO_3. The concentration of L varies from 0.25 to 4.00 M, and one must therefore expect large variations of the activity coefficients of reactants and products. These have not been taken into account by the authors who report equilibrium constants for the formation of five chloride complexes and six nitrate complexes that are listed in Table A-24. There is no information on the temperature of the experiments; this review assumes that it is 20−25°C.

Table A-24: Equilibrium constants for the formation of Th(IV)-chloride and nitrate complexes at room temperature obtained by the cation exchange method.

Complex	β_n	Complex	β_n
$ThCl^{3+}$	1.60 M^{-1}	$Th(NO_3)^{3+}$	3.55 M^{-1}
$ThCl_2^{2+}$	0.16 M^{-2}	$Th(NO_3)_2^{2+}$	2.10 M^{-2}
$ThCl_3^{+}$	0.14 M^{-3}	$Th(NO_3)_3^{+}$	0.50 M^{-3}
$ThCl_4(aq)$	0.035 M^{-4}	$Th(NO_3)_4(aq)$	0.19 M^{-4}
$ThCl_5^{-}$	0.0035 M^{-5}	$Th(NO_3)_5^{-}$	0.032 M^{-5}
		$Th(NO_3)_6^{2-}$	0.0040 M^{-6}

These data can at best be used to estimate the first equilibrium constants, β_1; the other proposed constants have no chemical significance. It is of interest to compare these equilibrium constants with those obtained for Pu^{4+} by Grenthe and Norén [1960GRE/NOR] using the same method and the same ionic medium; they report β_1 = 1.4 and 5.5 for the chloride and nitrate systems, respectively (and also equilibrium constants for higher complexes that are not reliable as they are strongly influenced by medium effects). This review notes that the nitrate complexes are significantly stronger than the chloride complexes in agreement with the LAXS observations in [1991JOH/MAG]. However, in view of the large medium changes that occur, no equilibrium constants are selected. Figure A-13 and A-14 show the distribution diagrams calculated for the Th^{4+}-Cl^- and the Th^{4+}-NO_3^- systems using the constants given by [1964NAB/KUD2]. These show that the higher complexes ThX_n^{4-n}, $n > 2$, are formed only when the anion concentrations are larger than 1 M.

Figure A-13: Distribution diagram for the thorium-chloride system using the equilibrium constants from [1964NAB/KUD2]. The complexes ThCl_n^{4-n}, $n > 1$ are not accepted by this review and are best considered as fitting constants in the method used.

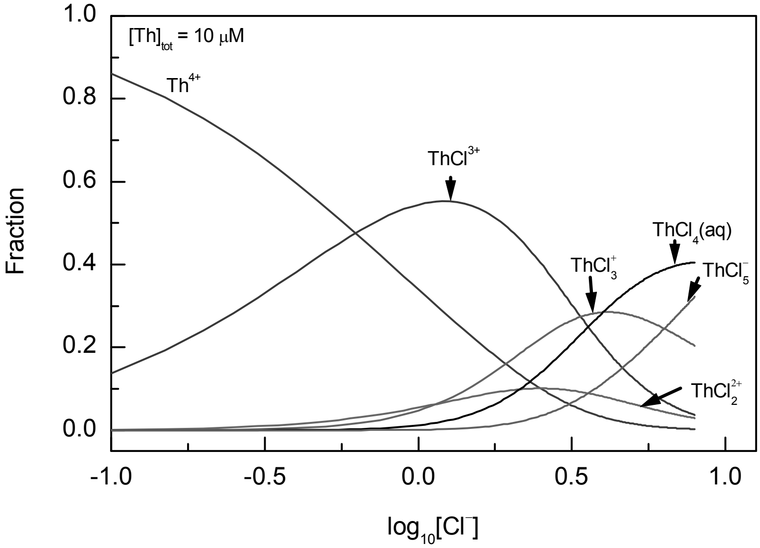
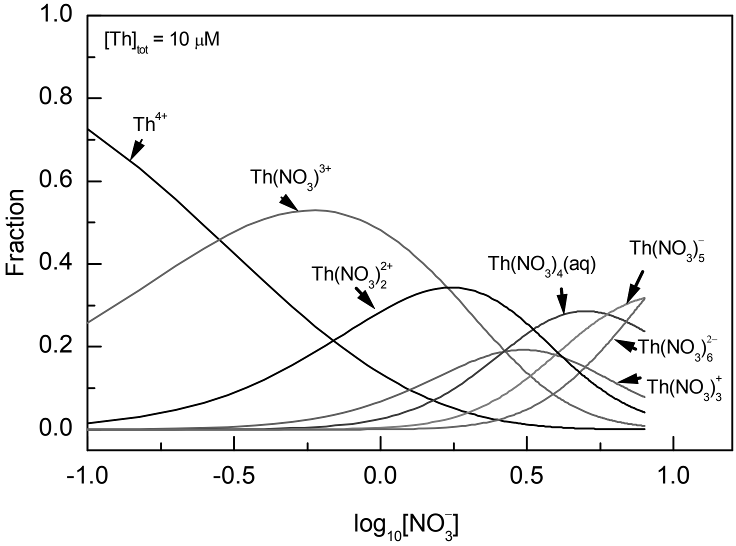


Figure A-14: Distribution diagram for the thorium-nitrate system using the equilibrium constants from [1964NAB/KUD2]. The complexes $\mathrm{Th(NO_3)}_n^{4-n}$, $n > 2$ are not accepted by this review and are best considered as fitting constants in the method used.



[1964SCA/WYL]

These authors have studied in detail the lower iodides of thorium using X-ray powder diffractometry, differential thermal analysis and microscopic examination.

Electrolytic thorium metal samples, containing 100 − 104 ppm oxygen, 6 − 15 ppm nitrogen, 5 − 6 ppm hydrogen, less than 600 ppm chlorine, and insignificant amounts of other impurities were used as starting material, together with iodine purified by distillation and condensation in a vacuum. High purity thorium obtained by the carbide-iodide process was also used for the critical experiments. It contained less than 25 ppm of each carbon, oxygen and nitrogen. The thorium tetraiodide used in the synthesis of the lower iodides was obtained by direct combination of the elements in Pyrex containers, and used after sublimation *in vacuo*.

The lower iodides were obtained by reacting, in tantalum or platinum containers, the tetraiodide and thorium metal (reduced to a powder form by several hydriding-dehydriding cycles) in the appropriate ratios. All transfers, weighings, and other operations were carried out in an evacuable glove box whose argon atmosphere could be maintained at a dew point of 213 K or better. Essentially conventional powder X-ray diffraction, microscopy and DTA techniques were used. Through the use of classical wet analytical methods, the I/Th molar ratios accurate to ±0.02 were reported for the various di-and triiodides samples, including those submitted to thermal analysis.

The α and β (high temperature) forms of ThI_2 were indexed on the basis of two distinct hexagonal cells, with a = 8.00 Å and c = 7.87 Å for the α form, and a = 9.21 Å and c = 3.74 Å for the β form. The structure of the β form has since been more definitely determined by [1968GUG/JAC], based on single crystal data.

The differential thermal analysis results leading to a tentative Th-I phase diagram show that ThI_3(cr) and ThI_2(cr) undergo peritectic transformations as follows: ThI_3 into β-ThI_2 and liquid at 1019 K and β-ThI_2 into Th metal plus liquid at 1137 K; in each case, the liquid has a I/Th ratio substantially less than 4. The transformation of α- to β-ThI_2 occurs sluggishly at 873 to 973 K. The existence of another iodide of Th at I/Th *ca.* 3.3 − 3.4 suggested subsequently by [1967GER/KRU] is considered as doubtful by [1964SCA/WYL].

[1965ARO/SAD]

The chemical potential of thorium relative to Th(cr) were calculated from the emf measurements in the single phase monocarbide region between $ThC_{0.66}$ and $ThC_{0.96}$. The cells were of the type Th, $ThF_4|CaF_2|ThF_4$, ThC_x,. Measurements were made at 1073 to 1223 K. The chemical potential at 1173 K decreases from − 1.7 kJ·mol^{-1} at $ThC_{0.66}$ to – 83.3 kJ·mol^{-1} at $ThC_{0.96}$. The thermodynamic data are discussed in connection with theories of chemical bonding.

These results are of limited interest for the present review, and are mentioned for information only.

[1965BAE/MEY]

The hydrolysis of Th(IV) has been studied at 0 and 95°C in 1 m (Na)ClO_4 using potentiometric titration technique. In addition the experimental data in [1954KRA/HOL] have been re-evaluated using the same least-squares method as the 0 and 95°C data. This is a precise experimental study representing the state of the art. The authors have checked the reversibility of their titrations and the possible occurrence of precipitation. They note that the equilibria are slowly attained in some test solutions and ascribe this to the formation of a hydrous oxide as a result of local high pH at the entry of the sodium hydroxide titrant. A transient precipitation usually occurred when an increment of base was added to thorium solutions. Normally this precipitate, produced by local excess of base, dissolves more or less readily on mixing, depending on the pH. No difficulty from this effect was noted in the measurements below $\bar{n}_{OH} = 1.8$ at 95°C; however, at 0°C it appeared that the precipitate so formed did not readily redissolve. The authors report their primary experimental data and also test a number of different chemical models (their Table IV). The complexes $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$ are always included in these models. Based on $\sigma(\bar{n}_{OH})$ they suggest that a minimum of five complexes is necessary to describe the experimental data. All of them contain $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$ and two other species, the composition of which was decided based on the least-squares fitting. The best additional species are $Th_3(OH)_6^{6+}$ and $Th_6(OH)_{15}^{9+}$ or $Th_4(OH)_8^{8+}$ and $Th_6(OH)_{15}^{9+}$; the latter were selected by the authors to describe the speciation at all temperatures investigated. The equilibrium constants are given in Table A-25. These equilibrium constants have also been evaluated with the LETAGROP least-squares program using the experimental data from [1954KRA/HOL]. The difference between the constants is much larger than the estimated standard deviations, indicating that the latter have to be treated with caution. The maximum concentration of $Th(OH)_2^{2+}$ is so small that this complex cannot be safely identified through these data.

Table A-25: Equilibrium constants, $-\log_{10}{}^*\beta_{n,m}(Th_m(OH)_n^{4m-n})$ for the "best" hydrolysis model based on data from [1954KRA/HOL] and [1965BAE/MEY] in 1 m (Na)ClO_4.

t (°C)	$-\log_{10}{}^*\beta_{1,1}$	$-\log_{10}{}^*\beta_{2,1}$	$-\log_{10}{}^*\beta_{2,2}$	$-\log_{10}{}^*\beta_{8,4}$	$-\log_{10}{}^*\beta_{15,6}$	$\sigma(\bar{n}_{OH})$
0	4.32 ± 0.02	8.48 ± 0.03	5.60 ± 0.02	22.79 ± 0.02	43.84 ± 0.02	0.0117
25	4.15 ± 0.04	7.70 ± 0.03	4.61 ± 0.02	19.01 ± 0.02	36.76 ± 0.02	0.0145
95	2.29 ± 0.02	4.50 ± 0.01	2.55 ± 0.03	10.49 ± 0.03	20.63 ± 0.02	0.0154

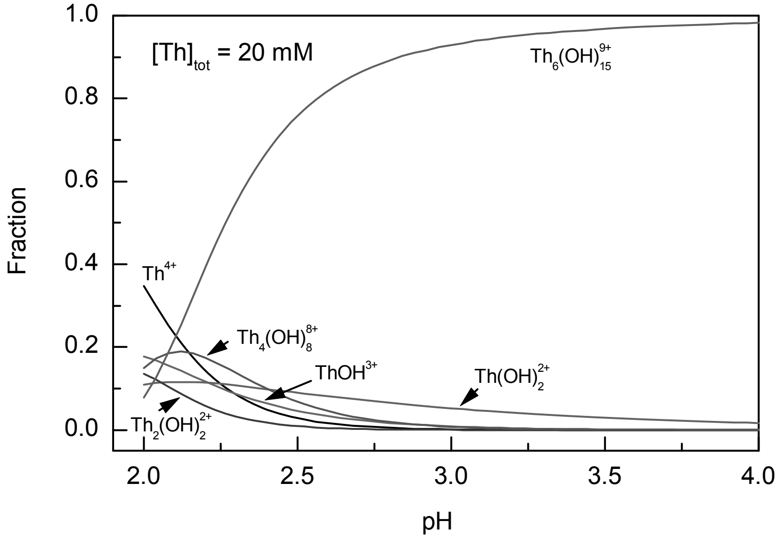
The enthalpy and entropy of reaction has been calculated from the temperature dependence of the equilibrium constants given in Table A-25. In the calculation the authors assumed a constant value of $\Delta_r C_{p,m}$. The results are given in Table A-26.

Table A-26: Enthalpy, entropy and heat capacity of reaction for the hydrolysis reactions of Th(IV) in 1 m (Na)ClO$_4$. In the last two columns are given the enthalpy and entropy of reaction divided by the number of OH-groups in the complex.

Species	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})	$\Delta_r C_{p,m}$ (J·K^{-1}·mol^{-1})	$\Delta_r H_m / n_{OH}$ (kJ·mol^{-1})	$\Delta_r S_m / n_{OH}$ (J·K^{-1}·mol^{-1})
$ThOH^{3+}$	25	4	937	25	4
$Th(OH)_2^{2+}$	58	46	1272	29	23
$Th_2(OH)_2^{6+}$	62	119	4	31	60
$Th_4(OH)_8^{8+}$	241	446	452	30	56
$Th_6(OH)_{15}^{9+}$	454	819	1000	30	55

It is not satisfactory to determine three parameters from three experimental data and the values given in Table A-26 should therefore be used with caution; the uncertainty estimated by the authors (about 1 kJ·mol^{-1} in $\Delta_r H_m$; and 80 J·K^{-1}·mol^{-1} in $\Delta_r C_{p,m}$) seems too optimistic. However, it is interesting to note that the enthalpy and entropy of reaction per OH-group is very nearly the same in all complexes and also similar to the values found for U(IV) [1962BAE/MEY]. The relative stability of the various complexes changes significantly with a change of temperature as seen by comparing the speciation diagrams in Figure A-21 at 25°C and in Figure A-15 at 95°C.

Figure A-15: The speciation in the Th(IV) hydroxide system at 95°C.



The experimental data also includes solubility measurements at 95°C; oversaturated Th solutions were spiked with crystalline $ThO_2(cr)$ and equilibrated for 10 to 100 days. The composition of the solid was identified by electron microscopy. Equilibrium was attained after ten days in test solutions with $-\log_{10}[H^+] = 2-2.6$, while test solutions in the range $-\log_{10}[H^+] < 2$ required longer equilibration times. The data were analysed and could be well described using the equilibrium constants for the two mononuclear complexes $ThOH^{3+}$ ($\log_{10} {}^*\beta_{1,1} = -2.26$) and $Th(OH)_2^{2+}$ ($\log_{10} {}^*\beta_{2,1} = -4.54$) from the potentiometric study at 95°C. The solubility constant $\log_{10} {}^*K_{s,0}$ (1.0 m $NaClO_4$, 95°C) = 4.26 is calculated for the reaction:

$$ThO_2(s) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O(l).$$

The solubility data in [1965BAE/MEY] are about 0.5−0.8 $\log_{10}$-units higher than those obtained by Rai *et al.* [2000RAI/MOO] in the same pH range in 0.1 M NaCl with a microcrystalline $ThO_2(s)$ solid, which resulted from the transformation of ThO_2(am, hyd) suspensions after heating for 52−76 days at 90°C. The difference might be due to ionic strength effects or to differences in crystallinity, *i.e.*, particle size.

[1965HEN/TYR]

This paper of Hentz and Tyree is discussed together with [1966HEN/JOH], a related paper from the same group.

These two communications present investigations of Th(IV) hydrolysis using ligh-scattering and ultracentrifugation. The light-scattering experiments have been made in the Th_{tot} range 10 to 100 mM at pH ranging from 2.07 to 3.25. The interpretation of the light-scattering data is at best qualitative as indicated by the statement in [1965HEN/TYR] that the species $Th(OH)(ClO_4)_2^+$ is formed at $\bar{n}_{OH} = 1$. At this value of $\bar{n}_{OH}$ a range of different polynuclear complexes is present in the test solutions, as shown by potentiometric and other equilibrium studies. At $\bar{n}_{OH}$ equal to 1.6 and 2.0 the average nuclearity is approximately 2.3 and 2.9, respectively, in qualitative agreement with the titration data. At higher values of $\bar{n}_{OH} \approx 3$, large aggregates with 140 to 150 Th atoms are formed, presumably colloids. The authors indicate that the observations at the lower values of $\bar{n}_{OH}$ refer to equilibrium systems, but that slow kinetics cannot be ruled out at higher pH. No equilibrium constants are reported. The ultra-centrifugation data [1966HEN/JOH] gives similar information as the light scattering data, but also in this case only the qualitative information that the nuclearity of Th(IV) complexes increases with increasing Th_{tot}; no equilibrium constants are reported. An important observation is that the polynuclear hydroxide complexes in chloride media are more prone to further aggregation (colloid formation ?) than the complexes formed in perchlorate media; this is in agreement with the break-down detection studies of Neck *et al.* [2002NEC/MUL], [2003BIT/MUL]. There is an extensive increase of aggregation with time in chloride media, while the perchlorate solutions do not change much over several years, particularly in solutions with $\bar{n}_{OH} < 1.5$.

[1965LIN2]

This contains a comprehensive compilation of published solubility data for thorium compounds prior to 1965. Raw experimental data for sulphate compounds of thorium from many different sources ([1910KOP/HOL], [1910BAR], [1911BAR], [1912BAR], [1912WIR]) are presented in this publication and were used by [1992FEL/RAI] and this review to determine $\Delta_f G_m^o$ values for several different solids important in Li_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, H_2SO_4, HCl and H_2SO_4 systems based on Pitzer and SIT models. For details see the review under [1910KOP/HOL] and main text, Section IX.1.3.3.

[1965OLS/MUL]

The nitrogen decomposition pressures for of ThN_{1-x}(cr) to give Th(l) + N_2(g) were measured from 2689 to 3063 K. ThN was found to melt congruently at (3063 ± 30) K under a nitrogen pressure just under 1 bar. The presence of oxygen as an impurity in the ThN(cr) has a large effect on the melting point and decomposition pressure. The decomposition pressure-temperature relation for pure ThN is given by: $\log_{10}p/\text{bar} = 8.095 - 33{,}224/T + 0.958\times10^{-17}\,T^5$. These authors suggest that ThN(cr) has only a small homogeneity range.

[1965SCA/TUR]

This paper concerns the synthesis of thorium oxyiodide and its study by X-ray diffractometry, optical and electron microscopy, visible and infrared spectroscopy, and solution calorimetry leading to a determination of its enthalpy of formation.

The compound was synthesised by reaction of thorium dioxide with a 20% excess molten thorium iodide. Most of the excess thorium iodide was sublimed from the product. Analytical results yielded 45.5% Th and 51.41% I (theoretical 46.2% Th and 50.6% I). The X-ray powder diffraction pattern was given but the data could not be indexed on the basis of a unit cell with orthorhombic or higher symmetry.

A value of − (169.9 ± 1.7) kJ·mol^{-1}, the average of four concordant measurements, was reported for the enthalpy of solution of the compound in 1 M HCl, after correction of individual measurements by 1.2 to 1.6 kJ·mol^{-1}, for the presence of 3 − 5 wt% thorium iodide in the oxyiodide. The amount of this impurity was determined by analysis for thorium and iodine of individual calorimetric solutions. For this correction, the authors used a “preliminary” value of −314 kJ·mol^{-1} for the enthalpy of solution of ThI_4(cr) in 1 M HCl. No further details on this value were given.

These results are the basis for the selection of the enthalpy of formation of $ThOI_2$(cr) by this review.

[1965SHC/SEM]

The total vapour pressures over the oxides ZrO_2, HfO_2, and ThO_2 were determined at *ca.* 2573 to 3023 K by isothermal evaporation and the partial pressures of the gaseous oxides MO_2(g) and MO(g) at these temperatures were established by mass spectroscopy on the basis of ZrO_2^+/ZrO^+ ratios. The following equations are given for the pressures of ThO(g) and ThO_2(g) over stoichiometric ThO_2(cr):

$$\log_{10} p_{\mathrm{ThO(g)}} / \mathrm{bar} = -33300 / T + 7.10 \qquad 2573-2973\ \mathrm{K}$$

$$\log_{10} p_{\mathrm{ThO_2(g)}} / \mathrm{bar} = -35180 / T + 7.87 \qquad 2573-2773\ \mathrm{K}$$

These data are discussed in Sections VII.1.1.2 and VII.1.3.2.

[1965TAK/WES2]

The heat capacity of a sample of thorium dicarbide was measured by adiabatic calorimetry from 5 to 350 K and was found to be of normal sigmoid shape without transitions or thermal anomalies. The sample was a composite of seven different samples, prepared from the elements and annealed at 5 h at 2273 K, crushed and reheated to “above 2273 K” for a further 5 h to obtain a sample of uniform composition. The C/Th ratio was analysed to be (1.98 ± 0.03), the major impurity being 0.79 wt% carbon, for which the heat capacities were corrected. There is no mention of oxygen contamination or analysis. At 298.15 K, the values of $C^{\circ}_{p,\mathrm{m}}$ for $ThC_{1.98}$ and (S°_{m} (298.15 K) − S_{m} (0 K)) are (56.9 ± 0.2) and (68.7 ± 0.3) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ respectively, where the uncertainties have been increased from the 0.1% quoted in the paper to account for uncertainties in the composition of the sample.

[1965WES/TAK2]

The heat capacity of arc-melted buttons of hypostoichiometric “ThC_2” was measured by adiabatic calorimetry from 6 to 346 K and was found to be of normal sigmoid shape without transitions or thermal anomalies. The calorimetric sample was a mixture from a series of analysed samples, prepared from the elements. The weighted overall composition of the mixed calorimetric sample was calculated from the analyses to be 96.91 mol% $ThC_{1.93}$, 2.43 mol% WC, 0.46 mol% ThO_2, 0.19 mol% “ThH_3” and 0.012 mol% Th_3N_4, for which the measured heat capacities were corrected. Of course, there is the possibility that some, at least, of the impurities were dissolved in the main dicarbide phase. At 298.15 K, the values of $C^{\circ}_{p,\mathrm{m}}$ for $ThC_{1.93}$ and (S°_{m} (298.15 K) – S_{m} (0 K)) are (56.7 ± 0.2) and (68.5 ± 0.3) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ respectively, where the uncertainties have been increased from the 0.1% quoted in the paper to account for uncertainties in the composition of the mixed sample.

[1966ALC/COR]

Mass-loss effusion studies have been made of the vaporisation of compounds of thorium and uranium with silicon and germanium, and of other compounds of U with Pb, Sn, In, and Ga. Gibbs energies of formation are reported for the compounds $ThSi_2$, Th_3Si_5, ThSi, Th_3Si_2 for the temperature range *ca.* $1685 < T < 1961$ K and $ThGe_3$,

$ThGe_2$, Th_3Ge_5, ThGe, Th_3Ge_2, and Th_3Ge for the temperature range *ca.* $1330 < T < 1500$ K. The data are presented only in graphical form and derived equations for the Gibbs energies of formation.

For all the alloys except that containing 37.5 at.% Si, corresponding to the phase field {liquid thorium, saturated with silicon + Th_3Si_2(cr)}, the pressures of thorium in the vapour were negligible. For this alloy, the individual pressures of Th(g) and Si(g) were measured by analysis of the condensed vapours, and the activity of thorium determined by comparing the measured p(Th) to that of their own measurements of the vapour pressure of pure thorium. However, there are no details of these measurements, merely a statement that the results were "in close agreement" with those of Darnell *et al.* [1960DAR/MCC]. It is noted in Section V.2.2 that the results of these authors are too high by a factor of three, probably because of residual oxygen contamination and consequent formation of ThO(g). This suggests that the Th-Si alloys used by Alcock *et al.* may also have contained appreciable oxygen, which would appear in the gas phase as both ThO(g) and SiO(g). In the absence of mass-spectrometric data, oxygen analyses or individual data values, it is impossible to correct for this effect, and it is preferable to use the thorium and silicon activities reported by Alcock *et al.,* rather than recalculate their results using the assessed data for the vapour pressures of the pure elements.

An additional source of uncertainty in the Th-Si study lies in the phase diagram at the temperature of the measurements. The authors found no evidence for separate phase fields due to the presence of Th_6Si_{11} as suggested by Brown and Norreys [1960BRO/NOR]. Alcock *et al.* interpreted their data in this region of the diagram in terms of one compound of composition Th_3Si_5, and we have also done this.

[1966ARO/AUS]

The authors report nitrogen pressures in the diphasic region ThN(cr) + Th_3N_4(cr) from *ca.* 1723 to 2073 K.

Samples of the nitride prepared by heating thorium metal in nitrogen at 773 to 1173 K had a N/Th molar ratio of (1.319 ± 0.002) as determined by the weight change. After correction for the 0.11 wt% oxygen present in the metallic thorium (assumed to form ThO_2(cr)), the composition of the thorium nitride becomes $ThN_{1.31}$. Aronson and Auskern [1966ARO/AUS] were not able to index the X-ray diffraction pattern obtained from the maroon-coloured product.

Nitrogen decomposition pressure measurements were made in the diphasic region ThN-Th_3N_4 from 1723 to 2073 K. The pressures ranged from 7×10^{-3} to 0.03 bar and equilibrium values were attained in (0.5 − 2) h. The pressures measured for both increasing and decreasing temperatures differed only slightly. The data were not sufficiently accurate to determine whether narrow ranges on non-stoichiometry exist in ThN and Th_3N_4, but there was some sluggishness in obtaining equilibrium in samples close to ThN.

No individual measurements are reported but the variation of $\log_{10} p_{\mathrm{N_2}} / \mathrm{bar}$ with reciprocal temperature given in their Figure 2, was accurately linear. The Gibbs energy expression for the reaction:

$$6\mathrm{ThN(cr)} + \mathrm{N_2(g)} \rightleftharpoons 2\mathrm{Th_3N_4(cr)} \qquad (\mathrm{A.51})$$

was calculated by the authors to be:

$$[\Delta_{\mathrm{r}} G_{\mathrm{m}}]^{2023\mathrm{K}}_{1723\mathrm{K}}\,((\mathrm{A.51}),\,T) = -\,(304.2 \pm 8.4) + (0.1368 \pm 0.0084)\,T\ \mathrm{kJ{\cdot}mol^{-1}}$$

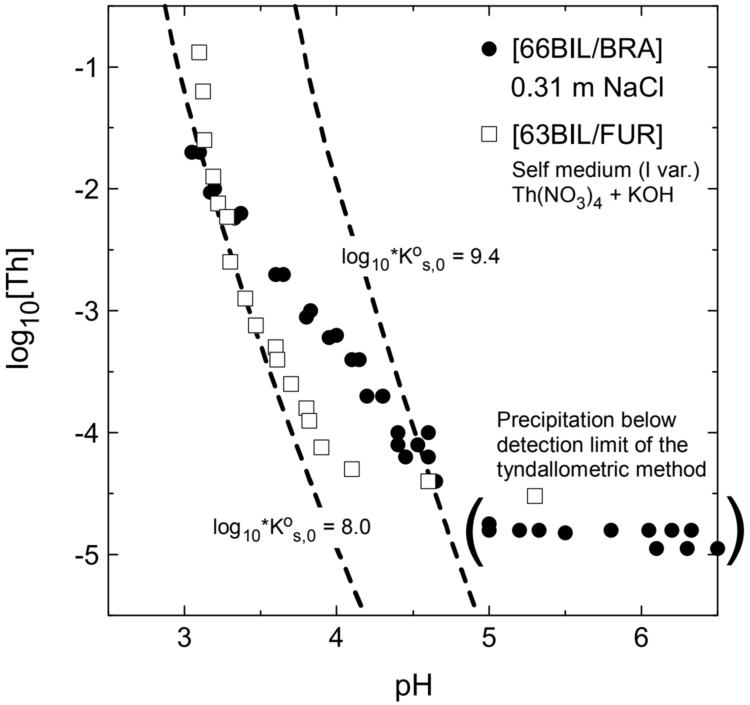
where the uncertainty includes those from experimental considerations as well as the reproducibility of the measurements. Both phases were assumed to be stoichiometric, which as noted in Section X.1.1.1 is probably true at the lower temperatures of the experimental range, but not, possibly at the higher temperatures.

[1966BIL/BRA]

This is a qualitative study of precipitation of zirconium and thorium in 50% seawater (salinity = 18.29‰; *ca.* 0.31 m NaCl), where the onset of precipitation was measured using a tyndallometric method. Bilinski and Branica [1966BIL/BRA] report "titration curves" where the onset of precipitation is measured as a function of pH and the total metal concentration ($[\mathrm{Th}]_{\mathrm{tot}} = 10^{-5} - 0.02$ M) at 20°C. The experimental data confirm the well known fact that these ions precipitate at low pH, lower for Zr (pH 1 − 3) than for Th (pH 3 − 5).

The authors did not determine equilibrium constants from their experimental data, but they show a solubility curve in Figure 2 of [1966BIL/BRA]. This curve is based on the pH values measured in the suspensions after 24 hours with a glass electrode calibrated against pH buffers (activity scale) and measurement of the total thorium concentration in the solution. As pH values might shift upon ageing of the suspensions (*cf.*, [1959HIG]) and the equilibrium thorium concentration after filtration or ultracentrifugation is certainly lower than $\mathrm{Th_{tot}}$; the solubility curve neither represents the correct pH at the onset of precipitation/colloid formation nor the classical solubility data from oversaturation. Nevertheless, using the hydrolysis constants and ion interaction coefficients selected in this review and $\log_{10} \gamma_{\mathrm{H^+}} = -0.12$ in 0.31 m NaCl as calculated with the SIT, re-evaluation of the data in [1966BIL/BRA] yields lower and upper limits for the solubility constant of thorium hydroxide ($8.0 \le \log_{10} {}^{*}K^{\circ}_{s,0} \le 9.4$). The mean value, $\log_{10} {}^{*}K^{\circ}_{s,0} = (8.7 \pm 0.7)$, is in reasonable agreement with the solubility constants recalculated by this review from numerous other studies. The constant level of $[\mathrm{Th}] = 1.6 \times 10^{-5}$ M at pH > 5 has no chemical significance, it simply reflects the detection limit of light scattering caused by solid particles, which was at $[\mathrm{Th}]_{\mathrm{tot}} = 3 \times 10^{-5}$ M for the equipment used by [1966BIL/BRA]. In an earlier study of Bilinski *et al.* [1963BIL/FUR], analogous experiments were performed in $\mathrm{Th(NO_3)_4}$-KOH "self media" without background electrolyte to keep ionic strength constant. For comparison they are also shown in Figure A-16.

Figure A-16: Solubility of thorium hydroxide determined by the tyndallometric method in 50% seawater [1966BIL/BRA] and Th(NO_3)$_4$-KOH solutions of variable ionic strength [1963BIL/FUR] at 20°C. The dashed lines are calculated for $I = 0.31$ mol·kg^{-1} (in aqueous NaCl) with $\log_{10}{}^{*}K^{\circ}_{s,0} = 8.0$ (lower limit) and 9.4 (upper limit) and the hydrolysis constants and ion interaction coefficients selected by this review.



[1966CHI/GAR]

The enthalpies of transformation and fusion of $ThCl_4$ (and several elements and alloys) were measured with an adiabatic calorimeter. Adequate adiabatic conditions were obtained by using a small external power source to compensate for a lack of temperature uniformity on the surface of the platinum radiation shield.

At fusion or transformation points, the thermal effect was determined by measuring, at constant power input to the sample, the time required to raise its temperature by 2 K.

The $ThCl_4$(cr) used, whose actual preparation was not described, was described as being *ca.* 99.8% pure, despite having as much as 1.5 mol% (1050 ppm) oxygen (possibly as $ThOCl_2$) and 0.1 mol% of each C and N and smaller amounts of Fe, Cr and Ni. Samples were sealed in tantalum containers, and premelted before the determinations. This will of course have removed much of the oxygen from the sample. There is also the possibility of the formation of lower chlorides, whose status is far from clear (see Section VIII.2.1). A solid-solid transition of unknown origin was observed at (679 ± 2) K, with an enthalpy of transition of (5.0 ± 1.0) $\text{kJ}\cdot\text{mol}^{-1}$ (three determinations). The melting point was found to be (1042 ± 2) K, and the enthalpy of fusion (61.5 ± 2.6) $\text{kJ}\cdot\text{mol}^{-1}$ (four determinations).

The enthalpies of fusion of ten other metals and alloys (plus $CaCl_2$) were also determined, and were within 5% of the literature values for these materials, except for Bi and Mg, where the deviations were 6.0 and 8.6%.

[1966GAN/KNA]

This is Knudsen-effusion study of the decomposition pressures of lead over the compounds in the Th-Pb system from 910 to 1263 K, depending on the phase field. The vapour pressure of pure lead was also determined from 908 to 1178 K. The mass losses of the cell during heating were measured by an automatically registering thermobalance. The decomposition pressures of the diphasic phase fields containing ThPb, $ThPb_2$, $ThPb_3$, and $ThPb_4$. The last compound was not previously recognised in the Th-Pb system. The measured vapour pressure of pure lead is in good agreement with the values derived from [1989COX/WAG]. The decomposition pressures in the various phase fields were combined with the vapour pressure of pure lead to provide Gibbs energies of formation of ThPb(cr), $ThPb_2$(cr), $ThPb_3$(cr), and $ThPb_4$(cr) from *ca.* 900 to 1300 K. As discussed in Section XI.5, 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.

[1966GIN/ARO]

Measurements on solid-state electrochemical cells with a CaF_2(cr) electrolyte were used to obtain thermodynamic data on thorium phosphides at 1073 to 1223 K. Two cells were studied: (I) Th, $ThF_4|CaF_2|ThF_4$, Th, $ThP_{0.55}$ and (II) Th, $ThF_4|CaF_2|ThF_4$, ThP, Th_3P_4. The emf of the first cell relates to the activity of thorium in the P-saturated metal, and is of no immediate interest to the review.

Th_3P_4(cr) was prepared from thorium and red phosphorus, and ThP by thermal decomposition of Th_3P_4(cr); their mixtures with ThF_4(cr) for the emf samples were annealed in tungsten or silica. Oxygen analyses by vacuum-fusion generally showed 600 − 800 ppm oxygen, but with one samples of $ThP_{0.96}$ as high as 1400 ppm; nitrogen and hydrogen levels were less than 100 ppm. Although appreciable (up to 2 mole%), such oxygen contamination should not be too important in the experiments with the second cell, since the overall P/Th should in general not be critical to the results.

The time required for stable emf values is not stated, except for a few values which were left for 7 − 15 h before measurement. Measurements made after both increasing and decreasing the temperature differed by of 2−3 mV in general, and the mean emf was adopted. However, the standard deviation of the emf cell (II) at the mid temperature was estimated to be as high as 11.4 mV, since there were noticeable differences in the emf for mixtures with P/Th ratios of 1.21, 1.15 and 1.01, particularly the last. This may be due to non-stoichiometry in 'ThP', or the greater effect of oxygen contamination near the stoichiometric composition of the monophosphide, or to slow attainment of equilibrium.

The detailed results are not reported, but for cell (II), the authors calculated the Gibbs energy of the cell reaction:

$$4\mathrm{ThP(cr)} \rightleftharpoons \mathrm{Th_3P_4(cr)} + \mathrm{Th(cr)} \tag{A.52}$$

to be:

$$[\Delta_\mathrm{f} G_\mathrm{m}]_{1073\mathrm{K}}^{1223\mathrm{K}}\,((\mathrm{A.52}), T) = -\,(224700 \pm 23400) + (38.9 \pm 31.0)\,T\ \mathrm{J{\cdot}mol^{-1}}$$

where the uncertainties are twice those quoted by the authors.

Of course, these results correspond to the oxygen saturated phosphides, which may not be exactly stoichiometric either.

The authors combined these data with the partial pressures of P_2(g) in the same diphasic region ThP(cr) + Th_3P_4(cr), over a much higher temperature range, to calculate the Gibbs energies of these phases. As noted in the Appendix A entry for [1963GIN/EFI], this review does not consider their results to be reliable enough, especially at the lower temperatures relevant to the combined analysis, for this to be a dependable procedure.

[1966HEN/JOH]

This paper of Hentz and Johnson is discussed together with [1965HEN/TYR], a related paper of the same group.

[1966HEU/EGA]

The Gibbs energy of formation of ThF_4(cr) was determined at 873 K with emf cells using a CaF_2 solid electrolyte and Mg/MgF_2(cr), Al/AlF_3, and Ni/NiF_2 counter electrodes. A silica cell was used for experiments with Mg/MgF_2 and Al/AlF_3 electrodes, but an all-nickel container was required for the cell with Ni/NiF_2. Separate experiments demonstrated that there was no electronic conduction in the CaF_2 solid electrolyte. Equilibrium was achieved only slowly, in 2−3 days. Measurements were made only at 873 K. The data are analysed by the third-law in Section VIII.1.1.2.3.

[1966LEV]

The enthalpy of Th(cr) and Th(l) relative to 310 K was measured in a drop calorimeter from 1269 to 1650 K for α-Th, from 1667 to 1991 K for β-Th and from 2069 to 2100 K for Th(l).

Analysis of the crystal-bar thorium used showed only trace amounts of some metallic elements and 50 ppm C and 90 ppm O. The calorimetric sample, a cylinder *ca.* 2.5 cm in diameter and 2.5 cm long, was sealed in a tungsten container. Tungsten appeared to be inert to Th(l) for a period of 2 h at 2100 K, the highest temperature reached. Temperatures were measured pyrometrically in a black-body hole bored in the tungsten container.

The data were consistent with the transition temperatures of 1653 and 2033 K reported earlier by Eash and Carlson [1960EAS/CAR], and these were used to calculate the enthalpies of transition and fusion, which were estimated to be (3590 ± 120) and (13800 ± 1250) J·mol^{-1} respectively. The enthalpy data were fitted to the equations:

$$H_m(T) - H_m(310) = -17140 + 36.510\,T\ (\text{J·mol}^{-1})\ \text{for } \alpha\text{-Th and}$$

$$H_m(T) - H_m(310) = 4515 + 15.702\,T + 5.795 \times 10^{-3}\,T^2\ \text{J·mol}^{-1}\ \text{for } \beta\text{-Th.}$$

The temperature range in the liquid region was too small to derive a meaningful heat capacity.

The uncertainty in the derived heat capacities was estimated by the author to be 1.5%.

[1966SU/NOV]

This paper deals mainly with the pressure and composition of the vapour in the KCl-$ThCl_4$ system, but does include six measurements of the vapour pressure of pure $ThCl_4$(cr) from 933 to 1043 K, by the boiling point method.

$ThCl_4$ was prepared by chlorination of thorium oxalate with a stream of chlorine saturated with CCl_4(g) at 923 to 973 K. It is described (in the English translation) as melting "at 669°C, very close to the 770°C given in tables", (the melting point selected by the review is 769°C), and unspecified analyses showed the Cl/Th ratio to be (3.98 ± 0.02).

The data, which are included in the discussion in Section VIII.2.1.4.1, are in excellent agreement with the corpus of other vapour pressure determinations for $ThCl_4$(cr).

[1966TAK/HON]

The phase diagram between Th and ThC was studied by metallographic and X-ray techniques and by measurements of the electrical resistivity in quenched and slowly-cooled Th-C alloys. The α-β transformation temperature of thorium increased gradually with carbon content up to 2.3 at% C, and rapidly thereafter. Extrapolation to zero carbon content gave T_{trs}(Th, cr) = (1633 ± 10) K.

[1967ARO]

Thermodynamic information on the various diphasic fields in the Th-S system was obtained from emf measurements on solid state cells, using CaF_2 as the electrolyte, at 1100 to 1200 K. The cells employed were:

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid Th(cr), ThS(cr), ThF_4(cr)$$

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid ThS(cr), Th_2S_3(cr), ThF_4(cr)$$

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid Th_2S_3(cr), Th_7S_{12}(cr), ThF_4(cr)$$

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid Th_7S_{12}(cr), ThS_2(cr), ThF_4(cr)$$

Steady emf values were attained only very slowly, especially for the two cells containing Th_7S_{12}(cr); moreover, the emf values varied appreciably (± 10mV) for different compositions in the same phase field, indications perhaps that equilibrium was not completely attained. This is often the case for solid-state emf reactions involving non-fluorides. For this reason we have quoted only the Gibbs energy values given by Aronson, rather then the enthalpies and entropies derived over a short temperature range.

The Gibbs energy obtained from the first cell relates to the activity of thorium in Th(cr) saturated with sulphur, and is of no importance for the review. The other cells involve the reactions listed below, with the corresponding Gibbs energy change at 1173 K.

$$Th(cr) + Th_2S_3(cr) \rightleftharpoons 3\ ThS(cr) \tag{A.53}$$

$$\Delta_r G_m\ ((A.53),\ 1173\ K) = -(82.8 \pm 8.2)\ kJ\cdot mol^{-1}$$

$$Th(cr) + Th_7S_{12}(cr) \rightleftharpoons 4Th_2S_3cr) \tag{A.54}$$

$$\Delta_r G_m\ ((A.54),\ 1173\ K) = -(166.1 \pm 8.2)\ kJ\cdot mol^{-1}$$

$$Th(cr) + 6ThS_2(cr) \rightleftharpoons Th_7S_{12}(cr) \tag{A.55}$$

$$\Delta_r G_m\ ((A.55),\ 1173\ K) = -(398.3 \pm 16.7)\ kJ\cdot mol^{-1}.$$

In the absence of any entropy or heat capacity data for the higher sulphides, no reliable data can be derived for Th_7S_{12}(cr) or ThS_2(cr), but since we have reasonably precise enthalpies of formation for ThS(cr) and Th_2S_3(cr), $\Delta_r G_m$ ((A.53), 1173 K) can be used to derive an approximate value for the entropy of Th_2S_3(cr). With the reasonable assumption that $\Delta_r C_{p,m}$ (A.54) is zero, the derived value is S^o_m (Th_2S_3, cr, 298.15 K) = (179.9 ± 18.0) $J\cdot K^{-1}\cdot mol^{-1}$ where the uncertainty excludes that from $\Delta_r C_{p,m}$ (A.54).

[1967BEN/HOF]

Parts of the Th-N phase diagram were determined by X-ray, microscopic, chemical, and thermal analyses of phases equilibrated with nitrogen (up to 3 bar) at temperatures up to 3093 K. The Th-ThN portion of the phase diagram is a peritectoid-peritectic system wherein, upon heating, the face centred cubic Th phase with a N:Th ratio (0.08 ± 0.02) decomposes peritectoidally at (1878 ± 20) K to body centred cubic Th and ThN. The body centred cubic Th phase with a N:Th ratio (0.09 ± 0.02) decomposes peritectically at (2073 ± 25) K to liquid Th and ThN. The Th-rich boundary of the ThN phase extends from the N:Th ratio (0.97 ± 0.03) at 1849 K to 0.87 at 2273 K, while the N-rich boundary extends from the N:Th ratio (1.03 ± 0.03) at 1888 K to 1.08 at 2338 K. The mononitride phase melts congruently at (3093 ± 30) K with the N:Th ratio (0.995 ± 0.005) under 2 atm $N_2(g)$, in agreement with the data of Olsen and Mulford [1965OLS/MUL]. The Th-rich boundary of the rhombohedral Th_3N_4 phase changes with increasing temperature from the N:Th ratio 1.33 at 1873 K to (1.29 ± 0.03) at 2233 K.

[1967BER]

Beran [1967BER] investigated the formation of mononuclear Th(IV) hydroxide complexes at 25°C by means of sorption onto two cation exchange materials (Katex S–4 and S–15) which differ only in their swelling properties. The experiments were performed at $I = 0.5$ M ($HClO_4$-$NaClO_4$) and low total thorium concentrations of 10^{-6} M, spiked with trace amounts of ^{234}Th for radiometric analysis. The author used glass and calomel reference electrodes for pH measurements. Details on electrode calibration and the transformation of the measured values into $-\log_{10}[OH^-]$ values used for data evaluation are not given in the paper. According to the ion product of water calculated with NEA-TDB auxiliary data ($\log_{10} K_w^o = -13.75$ in 0.5 M $NaClO_4$), the studies were performed in the range $-\log_{10}[H^+] = 1.0 - 3.5$.

In Figure 1 of [1967BER], the distribution coefficients $\log_{10} K_{S-4}$ and $\log_{10} K_{S-15}$

$$K = ([Th]_{sorbed} / [Th]_{aq}) (V_{sln} / m_{CE}) \qquad (A.56)$$

with V_{sln} = volume of solution and m_{CE} = mass of cation exchange material, are shown as function of $pOH = -\log_{10}[OH^-]$. It is evident that both the distribution coefficients $\log_{10} K_{S-4}$ and $\log_{10} K_{S-15}$ and also their dependence on pH are different. The two curves are not shifted in parallel but cross each other at $\log_{10}[OH^-] \approx -10.3$. This means that the differences between the distribution coefficients of the Th^{4+} ion (predominant at pH < 2, where $\log_{10} K_{S-4}$ and $\log_{10} K_{S-15}$ are approximately constant) and the hydroxide complexes are not the same in the two ion exchangers, as expected.

The authors calculated the average charge ($\bar{Z}$) of the dissolved thorium species $Th(OH)_n^{4-n}(aq)$, from the different values of K_{S-15} and K_{S-4} at given pH according to:

$$\bar{Z} = \{\log_{10}(K_{S-15}/K_{S-4}) / \log_{10}(V_{S-4}/V_{S-15})\} + 1 \qquad (A.57)$$

where V_{S-4}/V_{S-15} is a constant value (V = specific volume (mL) of swollen cation exchange materials S−4 and S−15 (mL) per gram of dry substance). The Th(IV) species are expected to be mononuclear at the low aqueous Th concentrations of about 5×10^{-7} M and pH < 3.5; however there seems to be no justification for Eq.(A.57). At a given pH the ratio between the overall distribution coefficients reflects differences in the individual distribution coefficients of the sorbed species and these values are known to vary with the cross-linking of the ion-exchanger. The calculated ratio will thus reflect the average charge of sorbed Th and not the average charge in solution. The stepwise equilibrium constants $\log_{10} K_n$ ($n = 1-4$) for the reactions:

$$\text{Th(OH)}_{n-1}^{4-n+1} + \text{OH}^- \rightleftharpoons \text{Th(OH)}_n^{4-n}$$

calculated by Beran from the plot of $\bar{Z}$ *vs.* pOH (Figure 2 in [1967BER]) are not reliable. The corresponding overall formation constants $\log_{10}{}^*\beta^\circ_{n,1}$, extrapolated to zero ionic strength with the SIT, are orders of magnitude higher than values from other studies accepted by this review.

Table A-27: Equilibrium constants $\log_{10} K_n$ and $\log_{10} \beta_{n,1}$ at $I = 0.5$ M ($HClO_4$-$NaClO_4$) and 25°C reported by Beran [1967BER]; $\log_{10} \beta^\circ_{n,1}$ and $\log_{10}{}^*\beta^\circ_{n,1}$ are extrapolated to $I = 0$ with the SIT by this review.

Complex	$\log_{10} K_n$	$\log_{10} \beta_{n,1}$	$\log_{10} \beta^\circ_{n,1}$	$\log_{10}{}^*\beta^\circ_{n,1}$
$Th(OH)^{3+}$	11.64 ± 0.07	11.64 ± 0.07	12.9 ± 0.1	− 1.1 ± 0.1
$Th(OH)_2^{2+}$	10.80 ± 0.07	22.44 ± 0.10	24.6 ± 0.2	− 3.4 ± 0.2
$Th(OH)_3^+$	10.62 ± 0.05	33.06 ± 0.11	35.8 ± 0.2	− 6.2 ± 0.2
$Th(OH)_4(aq)$	10.45 ± 0.07	43.51 ± 0.13	46.5 ± 0.2	− 9.5 ± 0.2

Nevertheless this paper is helpful to judge hydrolysis constants derived by cation exchange methods. The different pH-dependence of the sorption behaviour of Th(IV) onto different cation exchange materials shows that the evaluation of pH-dependent distribution (sorption) coefficients requires not only the fitting of the formation constants $\log_{10} \beta_{n,m}$ (or $\log_{10}{}^*\beta_{n,m}$) of the hydroxide complexes formed in solution but also of their equilibrium constants $\log_{10}{}^{\text{CE}}K_{n,m}$ for the sorption onto the cation exchange material (CE):

$$\text{Th}_m(\text{OH})_n^{4m-n}\,(\text{aq}) + \text{CE} \rightleftharpoons \text{CE}{-}\text{Th}_m(\text{OH})_n^{4m-n}\,(\text{sorbed}).$$

This is further corroborated by the cation exchange study of Davydov and Toropov [1986DAV/TOR2] at pH 1−4 ($I = 0.1$ M), where the distribution coefficients remain constant up to pH 3, whereas for the two cation exchange materials used by Beran [1967BER], Katex S–4 and S–15, the distribution coefficients begin to decrease already at pH > 2.5 and pH > 2.2, respectively.

[1967BIL/ING2]

Bilinski and Ingri [1967BIL/ING2] investigated the precipitation of thorium from aqueous solutions of thorium nitrate (1.25 mM) and ammonium oxalate (2.5−80 mM) at pH 1 to 10 and a temperature of 20°C. Ionic strength was kept constant at $I = 1.0$ M ($NaClO_4$). The H^+ concentration in the perchlorate solutions was decreased coulometrically and measured with a glass and a Ag/AgCl reference electrode. The precipitates formed, fluffy $Th(OH)_4(s)$ at pH 6−8 and $Th(C_2O_4)_2{\cdot}6H_2O(cr)$ at pH 1−2, were characterised by chemical analyses. The solubility of $Th(OH)_4(s)$ in the presence of oxalate and the potentiometric data in excess of oxalate were evaluated assuming simply the formation of one binary thorium oxalate complex:

$$Th(OH)_4(s) + 4\,C_2O_4^{2-} + 4H^+ \rightleftharpoons Th(C_2O_4)_4^{4-} + 4H_2O(l) \qquad (A.58)$$

$$Th^{4+} + 4\,C_2O_4^{2-} \rightleftharpoons Th(C_2O_4)_4^{4-} \qquad (A.59)$$

The calculated equilibrium constants, $\log_{10}{}^*K_{s,4}$ (A.58) = 34.8 and $\log_{10}\beta_4$ (A.59) = 24.2, respectively, are given without uncertainties. The difference between the two equilibrium constants yields a solubility constant of $\log_{10}{}^*K_{s,0}$ ($Th(OH)_4$, s, 1 M $NaClO_4$) = 10.6. However, as the simple aqueous speciation assumed for the investigated ternary solutions is not well ascertained, this solubility constant is not included in the final data selection. Data on the hydrolysis of Th(IV), as indicated by the title of the paper, are not given in [1967BIL/ING2], but in an earlier paper of Bilinski *et al.* [1963BIL/FUR].

[1967CHI/DOO]

The electrical resistivity of thorium rods containing 80−200 ppm of carbon, by weight, (plus 8−50 ppm N and 50−190 ppm O) were measured from room temperature to 1973 K, and the α-β transformation temperatures inferred from discontinuities in the resulting curves. Extrapolation of the measurements to zero carbon content indicates T_{trs} = (1623 ± 10) K for pure thorium. These results, showing that carbon raises the transformation temperature, are consistent with the phase boundaries established at much higher carbon contents.

[1967MER/SKO]

The solubility of $ThP_2O_7(s)$ was determined at 25°C in a 0.1 M $(Na,H)ClO_4$ ionic medium. The solid phase was characterised using elemental analysis before the experiments, but not after equilibrium had been attained. The concentration of H^+ in the various test solutions, as determined by the pH, varied between 100 and 5 mM and the corresponding solubility between 12.26×10^{-6} and 0.25×10^{-6} M. It is not clear how the solubility product and the formation of the equilibrium constant for the complex $ThP_2O_7(aq)$ have been determined; the authors point out that the concentration of $[ThP_2O_7(aq)]$ is constant in the presence of the solid phase of the same composition. They report the following equilibrium constants:

$$\log_{10} K_{s,0} = -(24.25 \pm 0.02) \text{ and } \log_{10}\beta_1 = (18.0 \pm 0.2),$$

for the reactions:

$$ThP_2O_7(s) \rightleftharpoons Th^{4+} + P_2O_7^{4-}$$

and

$$\mathrm{Th^{4+} + P_2O_7^{4-} \rightleftharpoons ThP_2O_7(aq)}$$

where the uncertainties are those given by the authors. The equilibrium constants depend on the auxiliary data used and the dissociation constants of pyrophosphoric acid used differ substantially from those selected in the present review. In addition the authors have not tested other equilibrium models than the one proposed; in particular they have not considered the possible formation of ternary complexes $\mathrm{ThH}_p(\mathrm{P_2O_7})_q$ (charge omitted for simplicity). For these reasons this review has not accepted the proposed equilibrium constants.

[1967MOS/ESS]

The authors have measured the solubility of $\mathrm{Th(HPO_4)_2{\cdot}4H_2O(s)}$ and $\mathrm{U(HPO_4)_2{\cdot}4H_2O(s)}$ in $\mathrm{HClO_4}$ solutions by varying the total concentration of phosphoric acid from 0.1 mM to 1.5 M at a constant hydrogen ion concentration of 0.35 M. There is no information about the temperature used and this review assumes that these data refer to "room temperature" around 20°C; there is no information about the characterisation of the solid phase, but this is well known and the present review has therefore accepted the procedures used. The experimental solubility for $\mathrm{U(HPO_4)_2{\cdot}4H_2O(s)}$ fits well to a smooth solubility curve (Figure 1 in [1967MOS/ESS]) indicating that the experimental procedures used are satisfactory. As the experimental data have been made at constant $[\mathrm{H^+}]$ it is not possible to determine the stoichiometry of the complexes with respect to $\mathrm{H^+}$. The reported conditional constants are valid at $[\mathrm{H^+}] = 0.35$ M. The reported equilibrium constants, $\log_{10}\beta_n$, for the reactions:

$$\mathrm{Th^{4+}} + n\,\mathrm{HPO_4^{2-}} \rightleftharpoons \mathrm{Th(HPO_4)}_n^{4-2n} \qquad n = 1-3$$

are $\log_{10}\beta_1 = 10.6$, $\log_{10}\beta_2 = 22.6$ and $\log_{10}\beta_3 = 31.3$, respectively. The value of $\log_{10}\beta_2$ is doubtful according to the present review as it would imply that the bonding strength of the second ligand is larger than that of the first and this is a very unusual situation that is not encountered in the other actinide(IV) complexes discussed in [1967MOS/ESS]. The solubility product for $\mathrm{Th(HPO_4)_2{\cdot}4H_2O(s)}$ is $\log_{10}K_{s,0} = -26.89$, considerably smaller than the value $\log_{10}K_{s,0} = -21.0$ (-19.9 for the experiments using a Th tracer) proposed in [1956CHU/STE] in sulphuric acid, but the agreement is better with their reported value in nitric acid, $\log_{10}K^{\circ}_{s,0} = -(26.6 \pm 0.2)$. In the latter study the effects of phosphate (and sulphate) complexation on the solubility were not taken into account. The experimental data in [1967MOS/ESS] are satisfactory, but as the stoichiometry with respect to $\mathrm{H^+}$ is not known, the reported equilibrium constants are not accepted by this review.

[1968DAN/MAG]

This potentiometric study uses the methodology and data analysis as described in [1954HIE] and [1964HIE/SIL] but the experimental concentration range is extended to higher thorium concentrations, up to 0.5 M Th(IV). The authors have chosen to change the proton concentration in the test solutions by adding 2 M NaOH. This is unfortunate due to the risk of local precipitation of hydrous oxides; they also note that the reproducibility of the experimental data is poor at $\bar{n}_{\mathrm{OH}} > 1$. Nevertheless the data analysis has been made using all the experimental information. The experiments have been made at 25.0°C using 4 M $\mathrm{NaNO_3}$ and 4 M $\mathrm{NaClO_4}$ as ionic media. In the $\mathrm{NaNO_3}$ medium the $\mathrm{Th_{tot}}$ concentrations vary between 0.01 and 0.5 M, the $-\log_{10}[\mathrm{H^+}]$ range between 2 and 3.5 and $\bar{n}_{\mathrm{OH}}$ from 0.05 to 1.4; in the $\mathrm{NaClO_4}$ medium $[\mathrm{Th}]_{\mathrm{tot}}$ varies between 0.05 and 0.5 M, the $-\log_{10}[\mathrm{H^+}]$ range between 2 and 3.5 and $\bar{n}_{\mathrm{OH}}$ between 0.05 and 1.9. The ionic medium composition changes significantly at the highest thorium concentrations. The highest $\bar{n}_{\mathrm{OH}}$ values are obtained in the $\mathrm{NaClO_4}$ ionic medium. The graphical analysis using the "core and links" model is not consistent with the least-squares model as previously found by Hietanen and Sillén [1964HIE/SIL] and only the least-squares equilibrium constants are therefore listed in Table A-28.

Table A-28: Equilibrium constants $\log_{10}{}^{*}\beta_{n,m}$ ($\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$) for the formation of Th(IV) hydroxide complexes for each ionic medium at 25°C.

Complex $\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$	$\log_{10}{}^{*}\beta_{n,m}(4\ \mathrm{M\ NO_3^-})$	$\log_{10}{}^{*}\beta_{n,m}(4\ \mathrm{M\ ClO_4^-})$
$\mathrm{Th_2(OH)^{7+}}$	-	-2.72 ± 0.09
$\mathrm{Th_2(OH)_2^{6+}}$	-5.49 ± 0.04	-
$\mathrm{Th_3(OH)_5^{7+}}$	-	-12.42 ± 0.05
$\mathrm{Th_2(OH)_4^{4+}}$	-	-10.49 ± 0.02
$\mathrm{Th_3(OH)_6^{6+}}$	-17.92 ± 0.07	-
$\mathrm{Th_4(OH)_8^{8+}}$	-	-19.23 ± 0.11
$\mathrm{Th_6(OH)_{14}^{10+}}$	-	-36.23 ± 0.13
$\mathrm{Th_4(OH)_{12}^{4+}}$	-37.21 ± 0.06	-

The equilibrium constants in perchlorate media proposed by Danesi *et al.* are in poor agreement with those of other authors, even though they describe their own experimental data well. This is another example of the difficulty in assigning a unique chemical model for the Th(IV) hydrolysis using potentiometric data alone. As the primary experimental data are only given as graphs of $\bar{n}_{\mathrm{OH}}$ *vs.* $-\log_{10}[\mathrm{H^+}]$ it has not been possible to test them against the models suggested in [1964HIE/SIL] and [1965BAE/MEY]. In the 4 M nitrate medium, the equilibrium constant for the (2,2) species is in good agreement with the measurements in [1982MIL/SUR2] in 0.5−3.0 M $\mathrm{NaNO_3}$ and the equilibrium constant for the (8,4) species is consistent with the value from [1991GRE/LAG2] in 3.0 M $\mathrm{NaClO_4}$. The value for the (12,4) complex in 4 M $\mathrm{NaNO_3}$ is compatible with the values reported in 0.1 M $\mathrm{KNO_3}$ [1983BRO/ELL] and 3.0 M $\mathrm{NaClO_4}$ [1991GRE/LAG2], *cf.*, Section VII.3.4.1.

[1968GIN]

Mass-spectrometric measurements were made on a nitrogen-containing Th-B-P alloy, contained in a tungsten crucible, but at two temperatures only, 2702 and 2745 K. The alloy was formed from a mixture of ThP and BN, but most of the nitrogen had been lost during earlier experimentation. Ion currents were converted to pressures using a silver calibration.

The authors combine the above reaction enthalpies with published thermodynamic data to give the dissociation energy D^{o} (298.15 K) and the enthalpy of formation, $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (298.15 K) of ThN(g) of (577.4 ± 33.5) and (470.7 ± 31.4) kJ·mol^{-1} respectively. The required thermal functions for ThP(g) and ThN(g) were estimated from those of US(g) and ThO(g) respectively. The only values quoted are of $((G_{\mathrm{m}} - H_{\mathrm{m}}(298.15\ \mathrm{K}))/T$ at 2500 and 3000 K.

These data have been recalculated by the review in Section X.1.1.2, but because of the paucity of the experimental data, and the various assumptions in the derivation, no data have been selected for ThN(g).

[1968GOL/KAL]

The complex formation in the Th(IV)-nitrite system was investigated using conductometry, spectrophotometry and polarography in methanol. The composition and equilibrium constants for ternary complexes $\mathrm{Th(OMe)_2(NO_2)^+}$, $\mathrm{Th(OMe)_2(NO_2)_2}$ and $\mathrm{Th(OMe)_2(NO_2)_3^-}$ were determined. These data are not relevant for estimates of nitrite complexes in aqueous solution.

[1968HIE/SIL]

This study of Th(IV) hydrolysis has been made in a 3.00 M (Na)Cl medium and a temperature of 25°C. The paper also includes a reinterpretation of experimental data from [1954HIE], [1954KRA/HOL] and [1965BAE/MEY]. The experimental method is the same as in [1954HIE] but with special care to reduce the amount of protolytic impurities, mainly iron, in the ionic medium. This is essential in order to increase the accuracy at the lowest values of $\mathrm{Th_{tot}}$, *cf.* p. 267 in [1968HIE/SIL]. The authors also used coulometric methods in order to avoid impurities and local $\mathrm{OH^-}$ excess in the titrations. The authors checked the reversibility of the system and that the potentials remained stable over time periods up to two weeks. The authors tested both glass- and hydrogen-electrodes and found the latter to be superior; all experimental data given in the paper refer to this electrode. The interpretation of the data and the testing of different chemical models were made using the least-squares method, LETAGROP developed by Sillén and his co-workers. Experimentally this study still represents the state of the art in potentiometric studies. The study covers a wide range of $\mathrm{Th_{tot}}$ concentrations, ten different concentrations from 0.10 to 100 mM, and a $-\log_{10}[\mathrm{H^+}]$ range from 2 to 4; $\bar{n}_{\mathrm{OH}}$ varied from 0 to about 1.7. The authors noticed that the potentials were not constant at the highest values of $\bar{n}_{\mathrm{OH}}$ and these data were left out in the analysis. At $\bar{n}_{\mathrm{OH}}$ around 1.5 the potential did not vary more than 0.2 mV over a two week period corresponding to a change in $-\log_{10}[\mathrm{H}^+]$ of about 0.003. The chemical models tested are given in Table A-29.

The "best" set of equilibrium constants is provided by Model III, but the difference between the different models is not large. In order to test the relative concentrations of the complexes in Model III, we have calculated the species distribution in two of the titrations and also explored possible structural models. From the distribution diagrams it is obvious that the predominant species are binuclear complexes $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_2(OH)_3^{5+}}$ and the hexanuclear complex $\mathrm{Th_6(OH)_{14}^{10+}}$. The trinuclear complex $\mathrm{Th_3(OH)_3^{9+}}$ is only present to a few percent in the test solutions, except at the highest total concentration of Th, where it amounts to about ten percent. Of the minor species suggested, the complex $\mathrm{Th_3OH^{11+}}$ seems unlikely on chemical grounds. Binuclear Th complexes have been identified both in solution and in the solid state [1968JOH], [1968JOH2], [1991JOH/MAG]; the hexanuclear complex may well have an octahedral $\mathrm{Th_6}$-core similar to that found in the uranium(IV) basic salt $\mathrm{U_6O_4(OH)_4(SO_4)_6}$, [1952LUN]; this review has not found any solid-state structures containing trinuclear hydroxide units. The other species found in the least-squares analysis may well be artefacts due to undetected systematic errors such as the formation of small amounts of larger polymers or colloids [2002NEC/MUL], [2003BIT/MUL], activity factor variations, *etc*.

The "best" chemical model is the one that gives the smallest least-squares residuals. The different models are shown in Table A-29. and the "best" speciation diagrams in Figure A-17. It is worth noting that the main difference between the models is found among the minor complexes, species that constitute only a few percent of the total concentration of Th(IV); this is shown in the speciation diagrams for some of the other models shown in Figure A-18, Figure A-19 and Figure A-20. It is instructive to compare the results given in Table A-29. In Model I we can note that the minor species (2,3) and (8,4) disappear when introducing a systematic error in $\bar{n}_{\mathrm{OH}}$, but that the effect on the major species is very small. Similar effects are also noticed in Models II-IV. Based on the least-squares analysis alone, Model III-B is the "best" one. The major species (1,1), (2,2) are present in all models, while several other combinations of complexes result in similar fit to the experimental data. It is obviously not straightforward to select the "best" chemical model and one must if possible use other criteria, such as the compatibility of the proposed stoichiometry with the known coordination chemistry of Th(IV). In our analysis we will remove minor species from consideration, as they are very strongly correlated with experimental artefacts.

Table A-29: The "best" combinations of equilibrium constants for Th(IV) hydrolysis in 3 M (Na)Cl as identified by a LETAGROP least-squares analysis. Model I has $m \leq 4$; Model II has $m \leq 5$; Model 3 $m \leq 6$ and Model IV no restrictions on m, where m is the the number of OH groups in the complex. In Models A no systematic errors are taken into account; in Models B the least-squares refinements have been made by assuming a systematic error in $\bar{n}_{\mathrm{OH}}$. The standard deviation $\sigma(\bar{n}_{\mathrm{OH}})$ is small but systematically smaller for the models with $m \leq 6$; these accordingly represent the "best" set of those investigated. Complexes that are poorly defined in the least-squares analysis have no estimated standard deviation in $\log_{10} {}^*\beta_{n,m}$. The typical systematic error in $\bar{n}_{\mathrm{OH}}$ is about 0.005 in Model III.

(n,m)		Model I-A	Model I-B
1,1	$\mathrm{ThOH^{3+}}$	– 4.60 ± 0.20	– 4.52 ± 0.13
1,2	$\mathrm{Th_2(OH)^{7+}}$	–	–
2,2	$\mathrm{Th_2(OH)_2^{6+}}$	– 4.83 ± 0.08	– 4.90 ± 0.06
3,2	$\mathrm{Th_2(OH)_3^{5+}}$	–	–
5,2	$\mathrm{Th_2(OH)_5^{3+}}$	–	–
1,3	$\mathrm{Th_3(OH)^{11+}}$	–	–
2,3	$\mathrm{Th_3(OH)_2^{10+}}$	– 4.05	–
3,3	$\mathrm{Th_3(OH)_3^{9+}}$	–	–
8,4	$\mathrm{Th_4(OH)_8^{8+}}$	– 20.97	–
9,4	$\mathrm{Th_4(OH)_9^{7+}}$	– 24.26 ± 0.11	– 24.22 ± 0.08
11,5	$\mathrm{Th_5(OH)_{11}^{9+}}$	–	–
12,5	$\mathrm{Th_5(OH)_{12}^{8+}}$	–	–
14,6	$\mathrm{Th_6(OH)_{14}^{10+}}$	–	–
25,10	$\mathrm{Th_{10}(OH)_{25}^{15+}}$	–	–
$\sigma\ \bar{n}_{\mathrm{OH}}$		0.044	0.030

(n,m)		Model II-A	Model II-B
1,1	$\mathrm{ThOH^{3+}}$	– 4.77 ± 0.18	– 4.57 ± 0.13
1,2	$\mathrm{Th_2(OH)^{7+}}$	–	–
2,2	$\mathrm{Th_2(OH)_2^{6+}}$	– 4.74 ± 0.06	– 4.90 ± 0.08
3,2	$\mathrm{Th_2(OH)_3^{5+}}$	–9.14	– 8.68 ± 0.12
5,2	$\mathrm{Th_2(OH)_5^{3+}}$	–	–
1,3	$\mathrm{Th_3(OH)^{11+}}$	–	–
2,3	$\mathrm{Th_3(OH)_2^{10+}}$	– 3.92 ± 0.24	– 4.53
3,3	$\mathrm{Th_3(OH)_3^{9+}}$	–	–
8,4	$\mathrm{Th_4(OH)_8^{8+}}$	–	–
9,4	$\mathrm{Th_4(OH)_9^{7+}}$	–	–
11,5	$\mathrm{Th_5(OH)_{11}^{9+}}$	– 28.56 ± 0.10	– 29.61
12,5	$\mathrm{Th_5(OH)_{12}^{8+}}$	– 32.56 ± 0.13	– 32.24 ± 0.10
14,6	$\mathrm{Th_6(OH)_{14}^{10+}}$	–	–
25,10	$\mathrm{Th_{10}(OH)_{25}^{15+}}$	–	–
$\sigma\ \bar{n}_{\mathrm{OH}}$		0.023	0.014

Table A-29 (continued)

(*n*,*m*)		Model III-A	Model III-B	Model III'-A
1,1	$\mathrm{ThOH^{3+}}$	– 5.23	– 5.14 ± 0.22	– 5.28
1,2	$\mathrm{Th_2(OH)^{7+}}$	–	–	– 2.64
2,2	$\mathrm{Th_2(OH)_2^{6+}}$	– 4.75 ± 0.05	– 4.78 ± 0.04	– 4.78 ± 0.06
3,2	$\mathrm{Th_2(OH)_3^{5+}}$	– 8.71 ± 0.10	– 8.72 ± 0.08	– 8.67 ± 0.10
5,2	$\mathrm{Th_2(OH)_5^{3+}}$	– 17.32	– 17.16 ± 0.14	– 17.39
1,3	$\mathrm{Th_3(OH)^{11+}}$	– 1.35 ± 0.23	– 1.50 ± 0.23	–
2,3	$\mathrm{Th_3(OH)_2^{10+}}$	–	–	–
3,3	$\mathrm{Th_3(OH)_3^{9+}}$	– 6.90 ± 0.20	– 6.86 ± 0.14	– 6.92 ± 0.23
8,4	$\mathrm{Th_4(OH)_8^{8+}}$	–	–	–
9,4	$\mathrm{Th_4(OH)_9^{7+}}$	–	–	–
11,5	$\mathrm{Th_5(OH)_{11}^{9+}}$	–	–	–
12,5	$\mathrm{Th_5(OH)_{12}^{8+}}$	–	–	–
14,6	$\mathrm{Th_6(OH)_{14}^{10+}}$	– 36.38 ± 0.04	– 36.42 ± 0.03	– 36.38 ± 0.04
25,10	$\mathrm{Th_{10}(OH)_{25}^{15+}}$	–	–	–
$\sigma\,\bar{n}_{\mathrm{OH}}$		0.015	0.011	0.016

(*n*,*m*)		Model IV-A	Model IV-B
1,1	$\mathrm{ThOH^{3+}}$	– 5.04 ± 0.25	– 4.97 ± 0.16
1,2	$\mathrm{Th_2(OH)^{7+}}$	–	–
2,2	$\mathrm{Th_2(OH)_2^{6+}}$	– 4.74±0.05	– 4.76 ± 0.04
3,2	$\mathrm{Th_2(OH)_3^{5+}}$	– 8.93	– 8.94 ± 0.20
5,2	$\mathrm{Th_2(OH)_5^{3+}}$	– 17.09 ± 0.18	– 16.99 ± 0.11
1,3	$\mathrm{Th_3(OH)^{11+}}$	– 1.19 ± 0.19	– 1.36 ± 0.18
2,3	$\mathrm{Th_3(OH)_2^{10+}}$	–	–
3,3	$\mathrm{Th_3(OH)_3^{9+}}$	– 6.86 ± 0.19	– 6.83 ± 0.13
8,4	$\mathrm{Th_4(OH)_8^{8+}}$	– 21.06	– 21.11 ± 0.22
9,4	$\mathrm{Th_4(OH)_9^{7+}}$	–	–
11,5	$\mathrm{Th_5(OH)_{11}^{9+}}$	–	–
12,5	$\mathrm{Th_5(OH)_{12}^{8+}}$	–	–
14,6	$\mathrm{Th_6(OH)_{14}^{10+}}$	– 36.56 ± 0.13	– 36.58 ± 0.10
25,10	$\mathrm{Th_{10}(OH)_{25}^{15+}}$	– 65.29	– 65.35 ± 0.21
$\sigma\,\bar{n}_{\mathrm{OH}}$		0.013	0.010

Figure A-17: Distribution diagram for the Th(IV)-hydroxide system in 3 M (Na)Cl, using the “best” set of equilibrium constants from Model III-B (Table A-29). Note that many of the complexes suggested there occur in such low concentrations that they are not seen in the figures.

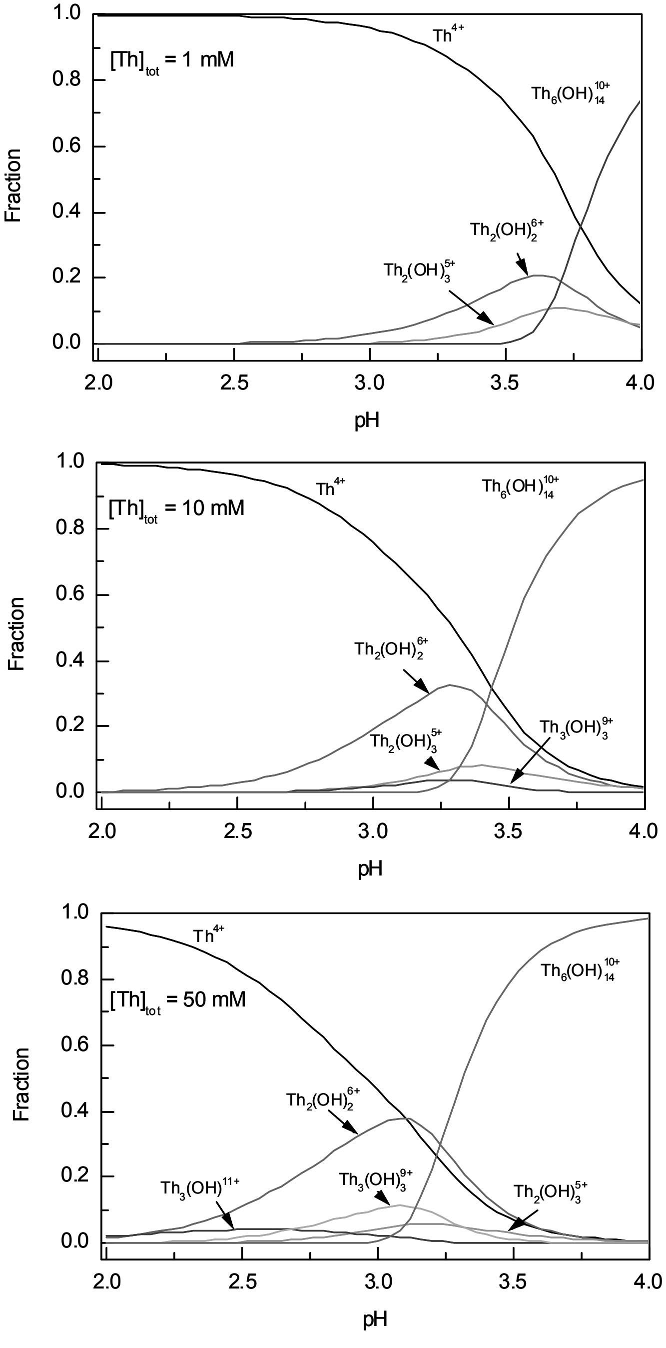


Figure A-18: Th(IV) speciation using Model I-A. The concentrations of species (1,1) and (2,3) are too low to be seen in the figure. The highest pH where precise data are obtained is around 3.2.

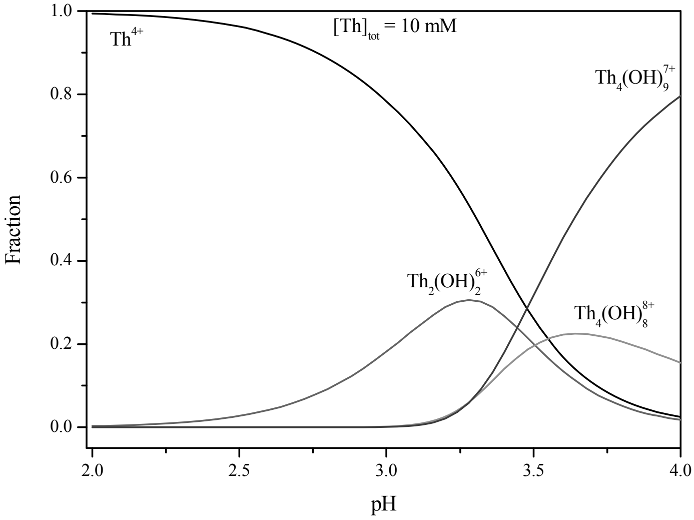


Figure A-19: Th(IV) speciation using Model II-A. The concentrations of species (1,1) and (2,3) are too low to be seen in the figure; the concentration of (3,2) is also low and its existence can hardly be considered established. The highest pH where precise data are obtained is around 3.2.

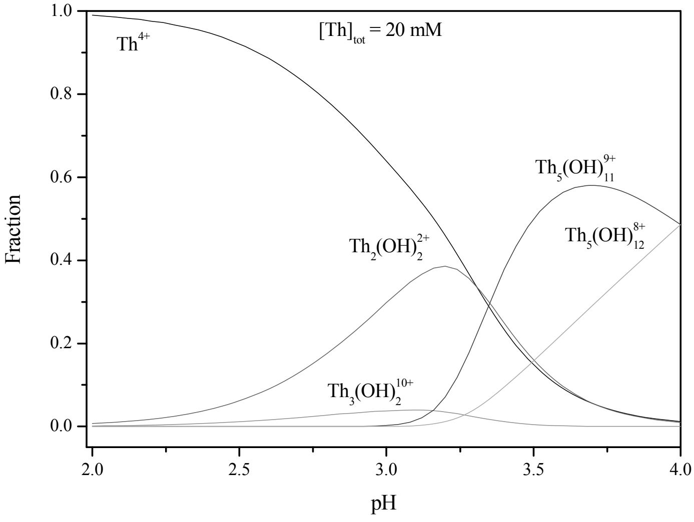
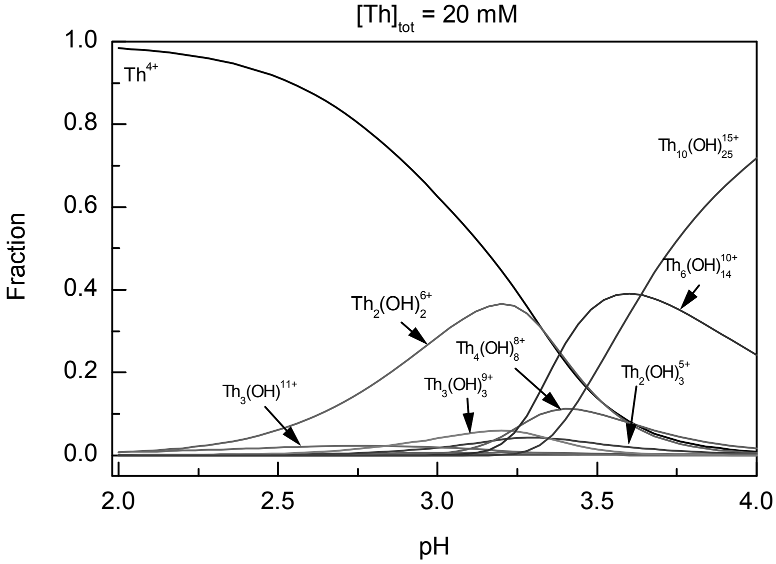


Figure A-20: Th(IV) speciation using Model IV-A; this model is very different from Models I and II. The highest pH where precise data are obtained is around 3.2.



This paper also contains a discussion and reinterpretation of experimental data in 1 M (Na)ClO_4 using the data from Hietanen [1954HIE], Kraus and Holmberg [1954KRA/HOL] and Baes *et al.* [1965BAE/MEY]. The comparison has been made using two different least-squares programs, LETAGROP and the Rush program from Oak Ridge. The data refer to a 1 M (Na)ClO_4 ionic medium and temperature 0, 25 and 95°C and the various equilibrium constants are given in Table A-30. The agreement between the different experiments is excellent, as indicated by the values of $\sigma(\overline{n}_{OH})$, despite the fact that they have been made in different laboratories and with slightly different potentiometric titration methods. It is also clear that the speciation model is very different from that found in 3 M NaCl. Another important difference is the $\overline{n}_{OH}$ range available before precipitation occurs; this is much larger in the perchlorate medium. This observation is important for the discussion of colloid/polymer formation [2002NEC/MUL], [2003BIT/MUL].

Distribution diagrams for Th(IV) in 1 M (Na)ClO_4 are shown in Figure A-21 using the data from [1954HIE] and Model B (Figure a) and the data from [1954KRA/HOL] with LETAGROP, Model B (Figure b). There is only a slight difference between the two least-squares programs, and no significant difference in the speciation. There is an error in Table 5 of [1968HIE/SIL], the entry for $Th_2(OH)_2^{6+}$ is placed in the column for the (2,1) complex. The equilibrium constant for $Th(OH)_2^{2+}$ from [1954KRA/HOL] and [1965BAE/MEY] is so small that no significant amount of this complex is present in the test solutions. This review has therefore not included this equilibrium constant when selecting the "best" set of equilibrium constants. The major species in both data sets are $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_4(OH)_8^{8+}}$ and $\mathrm{Th_6(OH)_{15}^{9+}}$. A comparison of the least-squares refinement of the same data using two different least-squares methods indicate that the standard deviations in the equilibrium constants is seriously underestimated.

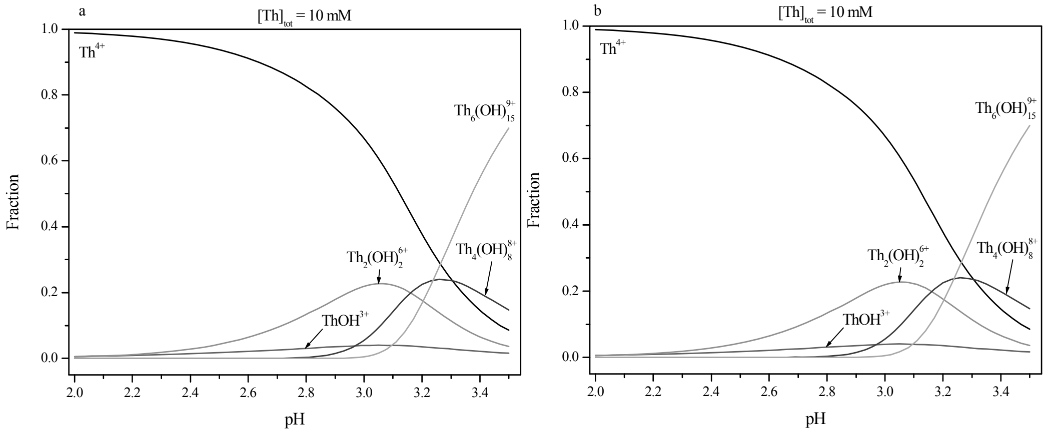
Additional discussion is given in the comments to [1954KRA/HOL] and [1965BAE/MEY].

Table A-30: Reinterpretation by [1968HIE/SIL] of the hydrolysis data and the corresponding equilibrium constants ($\log_{10} {}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ for Th(IV) in 1 M (Na)ClO$_4$ from [1954HIE], [1954KRA/HOL] and [1965BAE/MEY]. In Model A the data have been used without assumptions of a systematic error in $\bar{n}_{OH}$; in Model B such an error has been refined using the least-squares program LETAGROP; Oak Ridge denotes the least-squares program developed by Rush at Oak Ridge.

(1,1)	(2,1)	(2,2)	(8,4)	(15,6)	σ($\bar{n}_{\mathrm{OH}}$)	Data from Ref.	t
$\mathrm{Th(OH)^{3+}}$	$\mathrm{Th(OH)_2^{2+}}$	$\mathrm{Th_2(OH)_2^{6+}}$	$\mathrm{Th_4(OH)_8^{8+}}$	$\mathrm{Th_6(OH)_{15}^{9+}}$		Model	(°C)
– 4.33±0.07	– 8.48±0.10	– 5.60±0.06	– 22.79±0.05	– 43.84±0.06	0.012	[1965BAE/MEY] A	0
– 4.31±0.06	– 8.46±0.09	– 5.59±0.06	– 22.80±0.05	– 43.81±0.05	0.010	[1965BAE/MEY] B	0
– 4.32±0.02	– 8.48±0.03	– 5.60±0.02	– 22.79±0.02	– 43.84±0.02	0.012	[1965BAE/MEY] Oak Ridge	0
– 2.28±0.06	– 4.50±0.02	– 2.56±0.12	– 10.49±0.09	– 20.63±0.07	0.015	[1965BAE/MEY] A	95
– 2.25±0.03	– 4.51±0.02	– 2.59±0.08	– 10.44±0.05	– 20.61±0.05	0.009	[1965BAE/MEY] B	95
– 2.29±0.02	– 4.50±0.01	– 2.55±0.03	– 10.49±0.03	– 20.63±0.02	0.015	[1965BAE/MEY] Oak Ridge	95
– 4.21±0.13	– 7.72±0.07	– 4.61±0.06	– 19.15±0.01	– 37.02±0.06	0.015	[1954KRA/HOL] A	25
– 4.23±0.11	– 7.69±0.06	– 4.61±0.05	– 19.16±0.05	– 37.02±0.05	0.012	[1954KRA/HOL] B	25
– 4.15±0.04	– 7.70±0.03	– 4.61±0.02	– 19.01±0.02	– 36.76±0.02	0.015	[1954KRA/HOL] Oak Ridge	25
– 3.69±0.01	a	– 4.43±0.01	– 18.75±0.01	– 36.37±0.12	0.042	[1954HIE] A	25
– 3.71±0.08	a	– 4.44±0.07	– 18.78±0.08	– 36.42±0.08	0.028	[1954HIE] B	25

a: There is an error in Table 5 of [1968HIE/SIL] the equilibrium constant for the (2,2) species is erroneously given in the column for the (2,1) species.

Figure A-21: Speciation diagram using a) the data from [1954HIE] as reanalysed in [1968HIE/SIL] and b) the data from [1954KRA/HOL] as reanalysed by the chemical model from [1965BAE/MEY] using the LETAGROP least-squares program as described in [1968HIE/SIL].



[1968HUB/HOL2]

The enthalpies of formation of analysed samples of thorium carbides were obtained from combustion calorimetry in 25 atm oxygen at 298.15 K.

Samples of various stoichiometries were prepared by reacting in an arc furnace fully analysed thorium metal rods (99.7% purity) with spectrographic quality graphite rods, followed by remelting processes. From the full analysis of the samples given in Table A-31 hereunder their molecular composition could be calculated.

Table A-31: Analyses of the thorium carbide samples.

C/Th	0.75	0.81	0.91	1.00	1.91	1.91
wt%(Th)	96.00	95.8	97.82	98.54	99.22	99.77
wt%(C)combined	3.61	3.99	4.38	4.86	8.93	8.97
wt%(C)free	—	—	—	0.055	0.14	0.04
wt%(O)	0.37	0.18	0.24	0.161	0.066	0.016
wt%(N)	0.012	0.013	0.018	0.009	0.008	0.012
wt%(Si)	0.004	0.004	0.005	0.005	0.002	0.005

The main impurities were oxygen and nitrogen, which were assumed to be combined as ThO_2 (plus some SiO_2, and small amounts of metallic oxides) and Th_3N_4, respectively. The authors estimated that there is an uncertainty of ± 0.01 C/Th ratio in the formula of each compound.

Eight to ten combustion experiments were performed for each sample. Analytical results showed that the combustion of the samples averaged 97.8%.

After conversion to constant pressure and correction for impurities, the reported enthalpies of formation at 298.15 K are given in Table A-32.

Table A-32: Enthalpies of formation of ThC_x(cr).

x = C/Th	0.75	0.81	0.91	1.00	1.91	1.91
$-\Delta_f H_m^o$ (ThC_x, cr, 298.15 K) (kJ·mol^{-1})	69.4 ± 6.7	98.3 ± 3.8	118.8 ± 7.9	123.8 ± 4.6	124.3 ± 7.5	125.1 ± 5.4

[1968JOH], [1968JOH2]

The first of these studies is a single crystal X-ray investigation of the structure of $Th_2(OH)_2(NO_3)_6(H_2O)_8$(s), a compound that contains discrete binuclear complexes $Th_2(OH)_2(NO_3)_6(H_2O)_4$ containing double hydroxide bridges, resulting in a Th–Th distance of 3.99 Å, linking the Th atoms.

The nitrate ligands are coordinated through two oxygen atoms resulting in a first sphere coordination number of 11. This unusual coordination geometry is a result of the small ligand bite in the nitrate ligand. The structure provides important geometry information for the interpretation of large angle X-ray diffraction (LAXS) data from solutions containing hydrolysed Th(IV) complexes, the topic of the second study.

In [1968JOH2] Johansson studies the structure of Th test solutions with different ratio $OH^-_{tot}/Th_{tot} = \bar{n}_{OH}$ varying between 0 and 3 and at a total concentration Th_{tot} = 1.95 M. It is remarkable that these solutions remain clear (with the exception of a slight Tyndall effect at $\bar{n}_{OH} = 3$; the test solutions eventually solidify to form a glassy transparent substance. The experimental LAXS data were treated using standard methods that involve deconvolution to obtain a radial distribution curve, followed by least-squares fitting of different test models using the reduced intensity function to deduce the best model. It is not straightforward to obtain a structural model in this way as the structure has to be determined from one-dimensional data, that is the distances between pairs of atoms and number of such distances in the test solutions. The testing is facilitated by the fact that interactions involving Th are large in comparison with pair distances involving light atoms.

The test solutions used by Johansson contains several different hydroxide complexes and he has estimated the speciation using the equilibrium constants of Hietanen and Sillén [1964HIE/SIL]; this is obviously not correct due to the very large difference in composition and total concentration of Th(IV); however the information on the Th–Th and the Th–O distances in the first coordination sphere as a function of $\bar{n}_{OH}$ is certainly correct. Johansson reports values of the different pair distances and their frequency based on least squares fitting of the reduced intensity function, rather than using the radial distribution function. The data indicate that polynuclear complexes are formed, that the complexes contain coordinated nitrate and that the coordination number of Th(IV) is high and possibly decreases with increasing $\bar{n}_{\mathrm{OH}}$. The Th–Th distance at $\bar{n}_{\mathrm{OH}}$ = 0.69 is 3.99 Å in good agreement with the data from solid $\mathrm{Th_2(OH)_2(NO_3)_6(H_2O)_8(cr)}$; the distance decreases gradually and is 3.925 Å at $\bar{n}_{\mathrm{OH}}$ = 2.44. There is no significant variation in the Th–O distance as $\bar{n}_{\mathrm{OH}}$ varies.

This study does not provide any thermodynamic data but it confirms the formation of polynuclear complexes and that hydroxide bridging is an important structural element both in solution and the solid state.

[1968JUZ/GER]

A new modification of $\mathrm{Th_3N_4}$ was obtained by thermal degradation of $\mathrm{Th_2N_2(NH)}$ or by quenching samples prepared by heating $\mathrm{Th_3N_4}$ and $\mathrm{ThO_2}$. β-$\mathrm{Th_3N_4}$ has a monoclinically distorted $\mathrm{La_2O_3}$ lattice with $a = 6.952$, $b = 3.830$, $c = 6.206$ Å, $\beta = 90.71°$. It transforms monotropically to α-$\mathrm{Th_3N_4}$.

[1968OHA/MOR]

The reviewers have only been able to read the English abstract of this paper. The authors report equilibrium constants for chloride and nitrate complexes that have been determined using a potentiometric method. There are no details in the abstract and the experimental approach can therefore not be evaluated. However, potentiometric determination of the free ligand concentrations using a chloride sensitive electrode as used here is not very accurate for systems where weak complexes are formed. The nitrate system seems to have been investigated using the same method and measuring the competition between chloride and nitrate. This method is even less likely to provide accurate results. The experiments have been made at three different temperatures, 15, 25 and 35°C and in $\mathrm{KNO_3}$, $\mathrm{NaClO_4}$ and $\mathrm{NaNO_3}$ - $\mathrm{NaClO_4}$ media with concentrations ranging from 0.05 to 1.6 M. It is not clear from the abstract if the ionic strength has been kept constant, although the figures indicate that this might be the case. The authors find a significant ionic strength dependence of the equilibrium constants. For $\mathrm{ThCl^{3+}}$ the equilibrium constant decreases from 6 $\mathrm{M^{-1}}$ at I = 0.5 M, to 2.8 $\mathrm{M^{-1}}$ at I = 1.0 M; extrapolation to zero ionic strength gave an equilibrium constant of 37 $\mathrm{M^{-1}}$. The extrapolation to zero ionic strength seems to have been made without use of theory. In view of the limited information on experimental details, this review has not accepted the data provided by Ohashi and Morozumi.

[1968TED/RUM]

The authors have determined the equilibrium constants in the Th(IV)- $\mathrm{NO_3^-}$ system in a 2.0 M $\mathrm{H(NO_3,ClO_4)}$ ionic medium and a temperature of 25ºC, using cation exchange based on a method developed by Fronaeus [1951FRO] and adapted to $\mathrm{Pu^{4+}}$ by Grenthe and Norén; the latter study has been evaluated under [1960GRE/NOR] by Lemire *et al.* [2001LEM/FUG]. The reviewers in [2001LEM/FUG] pointed out that the large variation in the ionic medium composition necessary to study the weak Pu(IV) nitrate complexes in [1960GRE/NOR] made it impossible to decide if the experimental observations were due to activity factor variations or complex formation and they accepted only the equilibrium constant for the formation of $Pu(NO_3)^{3+}$. The equilibrium constants of Tedesco *et al.* are:

$$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+} \qquad \log_{10} \beta_1 = (1.22 \pm 0.03)$$

$$Th^{4+} + 2NO_3^- \rightleftharpoons Th(NO_3)_2^{2+} \qquad \log_{10} \beta_2 = (1.53 \pm 0.15)$$

$$Th^{4+} + 3NO_3^- \rightleftharpoons Th(NO_3)_3^{+} \qquad \log_{10} \beta_3 = (1.10 \pm 0.28).$$

The equilibrium constants in [1968TED/RUM], which refer to an ionic strength of $I = 2.0$ M $H(NO_3, ClO_4)$ and a temperature of 25°C, have been determined in test solutions where $[NO_3^-] < 0.5$ M. Extrapolation from $I = 2.2$ m to zero ionic strength using the ion-interaction constants in Table B-4 ($\Delta\varepsilon = -(0.21 \pm 0.17)$, $-(0.41 \pm 0.21)$ and $-(0.66 \pm 0.19)$ kg·mol^{-1} for n = 1, 2 and 3, respectively) yields $\log_{10} \beta_1^\circ = (2.59 \pm 0.37)$, $\log_{10} \beta_2^\circ = (3.83 \pm 0.49)$ and $\log_{10} \beta_3^\circ = (3.74 \pm 0.50)$.

This review has followed the evaluation of [1960GRE/NOR] in [2001LEM/FUG] on the analogous Pu^{4+}- NO_3^- system that only the equilibrium constant for the formation of the first nitrate complex can be determined. The value of $\log_{10} \beta_1^\circ = (2.59 \pm 0.37)$ is significantly larger than the values for the corresponding complexes in the U(IV), Np(IV) and Pu(IV) systems, (1.47 ± 0.13), (1.90 ± 0.15) and (1.95 ± 0.15), respectively. The value of $\log_{10} \beta_2^\circ = (3.83 \pm 0.49)$ is also considerably larger than the value for U(IV) ($\log_{10} \beta_2^\circ = (2.30 \pm 0.05)$ [1992GRE/FUG]). As the stability of complexes of complexes with a given ligand usually increases in the order Th(IV) < U(IV) < Np(IV) $\leq$ Pu(IV), this review does not accept the equilibrium constants given in [1968TED/RUM].

[1969BAC/BRO]

This is a large angle X-ray diffraction study of the structure of the Th^{4+} ion and of the structure of an hydroxide complex in test solutions formally described as containing $ThO(ClO_4)_2$. The experimental data are analysed using the radial distribution function and estimating the agreement of the experimental curve with that calculated using different structure models. The fitting has not used the least-squares approached used by Johansson [1968JOH2] and no quantitative comparison of different models has been made. The structure of Th^{4+} was made in test solutions containing 2.79 M $Th(ClO_4)_4$ and a large excess of $HClO_4$ to ensure that no hydrolytic species are present. The authors report pair interactions at 1.50 Å, due to Cl–O distances in the perchlorate ion, and one distance at 2.50 Å, presumably due to Th–OH_2 and O–O distances in the perchlorate ion, the latter equal to 2.40 Å. It is very difficult to deconvolute the radial distribution peaks, but the authors suggest a coordination number of 11 for the aquo ion. The uncertainty in the coordination number is large and the data are also compatible uncertainty in the coordination number is large and the data are also compatible with coordination numbers nine and ten.

The experiments in the hydrolysed test solutions were made at a total concentration of Th(IV) equal to 3.95 M, with an average number of two coordinated hydroxide ions per Th. The radial distribution curve contains a large narrow peak at 4.00 Å in addition to those in the test solution containing Th^{4+}. The integral of the 4.00 Å peak indicates pair interactions in a tetrahedral Th_4-unit and the authors suggest that this has the stoichiometry $Th_4(OH)_6^{10+}$, with the hydroxide bridges along the six edges in a tetrahedron. Another possibility that has not been discussed is a "cubane" core "$Th_4(OH)_4$" with one additional hydroxide coordinated to each Th, resulting in a $Th_4(OH)_8^{8+}$ stoichiometry as suggested in some potentiometric studies. A planar structure as in the "$Zr_4(OH)_8$"-core [1960MUH/VAU] has two different metal-metal distances and can therefore be excluded.

[1969BAS]

Finely divided thorium was treated with $PH_3(g)$ at 823 K to give $Th_3P_4(cr)$, which was mixed with further Th(cr) and heated *in vacuo* at 1473 – 1573 K to give $ThP_{0.99}(cr)$, with a lattice parameter of 5.833 Å. The apparent melting point under a helium atmosphere was 3173 K, but the author was unable to determine whether this was the true melting point, or the temperature of a eutectic with the tungsten container.

[1969DAH/GAN]

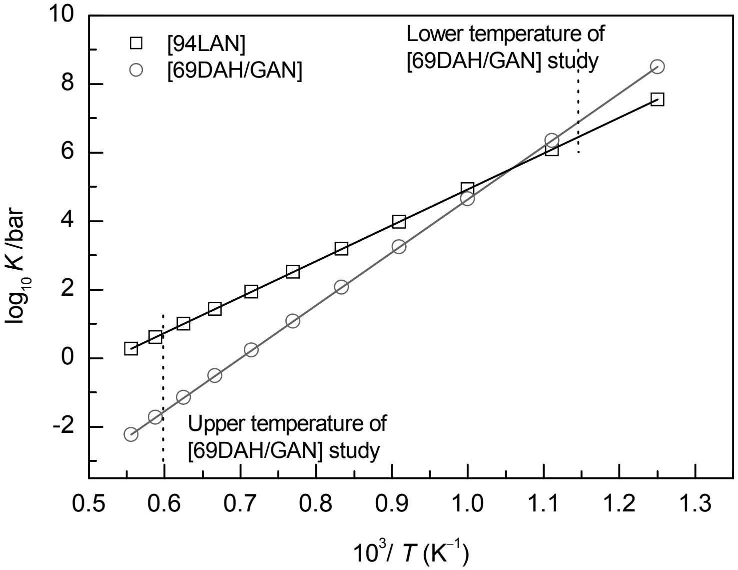
The dissociation pressure of bismuth in the system bismuth-thorium was determined using weight-loss Knudsen effusion between 884 and 1759 K. Isothermal dissociation curves and X-ray diagrams confirmed the stoichiometric compounds $ThBi_2(cr)$ and $Th_3Bi_4(cr)$. A homogeneity range from *ca.* $ThBi_{0.80}$ and $ThBi_{1.08}$ is indicated for the ThBi(cr) phase. The pressure measurements gave no indication of the compound Th_5Bi_3, although this is a well-established compound in the system. Equations are given for the values of $\log_{10}(p_{Bi} + p_{Bi_2})$ for the vaporisation of pure Bi and the dissociation pressures of bismuth in the univariant regions: liquid + $ThBi_2$, $ThBi_2$ + Th_3Bi_4, Th_3Bi_4 + $ThBi_{1.08}$, $ThBi_{0.8}$ + Th_3Bi and Th_3Bi + liquid.

The Th-Bi alloys were prepared from 99.999% Bi and nuclear grade Th (< 70 ppm impurities) in CaF_2 crucibles at 1073 K and annealed.

Lattice constant measurements obtained from X-ray data are given for $ThBi_2(cr)$ and $Th_3Bi_4(cr)$; these agree well with earlier values. Expressions for $\log_{10}(p_{Bi} + p_{Bi_2})$, $\log_{10}p_{Bi}$ and $\log_{10}a_{Bi}$ for the various Th-Bi phase fields are given.

However, there are a number of problems with this study. Since the vapour contains both $Bi_2(g)$ and Bi(g), it is necessary to know the relative proportions of each before the measured mass loss can be converted to the individual Bi(g) and $Bi_2(g)$ pressures. The authors used an expression for the dimerisation equilibrium constant they derived from the assessment by [1959GRO/LEV] and the torsion effusion study by [1963ALD/PRA]. These are reliable studies for the equilibrium constant but only for the temperature range around 1000 K, but the authors extrapolated the derived equation to 1673 K without change. The dimerisation constant calculated from the thermodynamic data for Bi(cr, l), Bi(g) and Bi_2(g) given in the Landolt-Bornstein tables [1994LAN], is compared with that used by [1969DAH/GAN] in Figure A-22. From this it is seen that although the dimerisation constant used by the authors is reasonably accurate around 1000 K, it markedly underestimates the fraction of Bi_2(g) in the vapour at higher temperatures – indeed by a factor as high as 150 at the highest temperatures used. Thus their calculated pressures of Bi(g) over pure Bi(l) will be appreciably too high at the higher temperatures. As a consequence, since the bismuth activities are calculated from the ratio of the derived p_{Bi} in a given phase field to that for pure Bi(l), their calculated activities will be too low at the higher temperatures. However, the compositions of the residual solid, which were calculated from the mass of bismuth lost from the initial samples, should not be affected.

Figure A-22: Dimerisation constant for $2Bi(g) \rightleftharpoons Bi_2(g)$



It should be noted that, although at higher temperatures, there are appreciable amounts of Bi_3(g) and Bi_4(g) in the vapour over pure Bi(l), in the study under discussion, the activities of bismuth in the system at the higher temperatures are so low that these species are no longer important.

Another problem with this study is that the experimental bismuth pressures are not consistent with the phase diagram in some areas. In particular there is no appreciable change in activity as the composition of the effusing solid passing through the Th_5Bi_3 composition, where there is well-established compound. Moreover, the authors found evidence for the formation of a thorium-rich phase with a composition around Th_3Bi(cr), but this phase has not been observed in any other studies. Dahlke *et al.* [1969DAH/GAN] also found that the monobismuthide phase has a considerable range of homogeneity, from $ThBi_{0.8}$ to $ThBi_{1.08}$, but again, there is no independent evidence for this. A further difficulty in processing the data from this study is that neither the solubility nor the activity of thorium in the melt in equilibrium with the most Bi-poor region was measured by the authors, so individual Gibbs energies of the Th-Bi compounds cannot be derived from this work alone (but see below).

Because of the inappropriate equation for the dimerisation reaction, all the results of Dahlke *et al.* have been completely re-evaluated from their raw data, using the data for the dimerisation constant calculated from the data given in [1994LAN], but from the total vapour pressures of pure Bi(l) measured by [1969DAH/GAN]. This helps to cancel any related experimental errors in the pressure measurements in the Th-Bi phase fields. The resulting bismuth activities in the various diphasic fields are shown in Figure A-23, which also includes the original values reported by [1969DAH/GAN]. It will be seen that at the higher temperatures, the recalculated bismuth activities are substantially lower than those given by the original authors, due, as noted above, to their overestimating the partial pressure of Bi(g) in the vaporisation of pure Bi(l).

The corresponding partial Gibbs energy of bismuth in these phase fields are given in Table A-33.

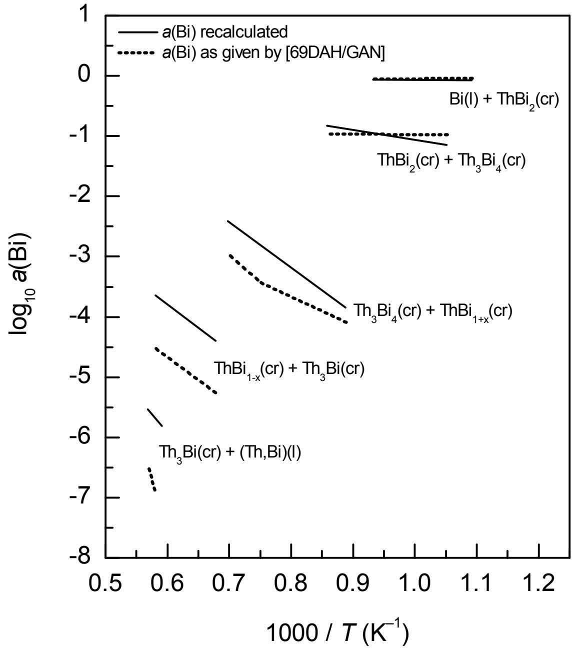
Table A-33: Bismuth potentials in the diphasic field in the Th-Bi system.

Phase field	$\Delta_{\text{sln}}G_{\text{m}}$ (Bi) ($\text{J·K}^{-1}\text{·mol}^{-1}$)	Temperature range (K)
(Th,Bi)(l) + Th_3Bi(cr)	$-237850 + 29.30\,T$	1691 − 1759
Th_3Bi(cr) + $ThBi_{1-x}$(cr)	$-147218 + 15.60\,T$	1474 − 1723
$ThBi_{1+x}$(cr) + Th_3Bi_4(cr)	$-144119 + 54.35\,T$	1126 − 1433
Th_3Bi_4(cr) + $ThBi_2$(cr)	$-31631 + 11.233\,T$	951 − 1165
$ThBi_2$(cr) + (Bi,Th)(l)	$-188 + 0.636\,T$	916 − 1073

The recalculated activities in the diphasic field Th_3Bi_4(cr) + $ThBi_2$(cr) from 950 to 1150 K can be combined with the Gibbs energy of formation of $ThBi_2$(cr) in a similar temperature range measured by Poyarkov *et al.* [1974POY/LEB] to give an estimate of $\Delta_{\text{f}}G_{\text{m}}$ (Th_3Bi_4, cr), as discussed in Section X.5. In principle, this could be extended to the remaining phase fields, but owing to uncertain phase boundaries of

ThBi(cr), and discrepancies with the phase diagram, this is not thought to be a meaningful proposition.

Figure A-23: Bismuth activities from [1969DAH/GAN], recalculated.



[1969GIN2]

Mass-spectrometric measurements were made on a Th-B-P alloy, contained in a tungsten crucible, but at only two temperatures, 2705 and 2804 K. Ion currents were converted to pressures by comparison with the $P_2(g) \rightleftharpoons 2P(g)$ equilibrium, using early JANAF data for these species.

The authors combine the third-law enthalpies of various reactions involving Th, Th_2, ThB, ThP, B, P, P_2 gaseous species with published thermodynamic data to calculate the dissociation energy D° (0 K) and the enthalpies of formation, $\Delta_f H^\circ_m$ (298.15 K), using estimated thermal functions for ThP(g) and ThB(g) from quoted estimated molecular parameters.

In view of the paucity of the experimental data, and the various assumptions in the derivations, no data have been selected for ThP(g), ThB(g) or $Th_2(g)$, but the relevant data have been re-evaluated in the relevant sections of the review for information only.

[1969KHA/MOL2]

The IR spectra of the solid phases: 1. $Na_6[Th(CO_3)_5]\cdot 12H_2O$; 2. $Na_6[Th(CO_3)_5]\cdot 20H_2O$; 3. $Th(OH)_2(CO_3)\cdot 2H_2O$; 4. $[C(NH_2)_3)_6][Th(CO_3)_5]\cdot 4H_2O$ and 5. $[Co(NH_3)_6]_2[Th(CO_3)_5]\cdot 4H_2O$ have been used to suggest the mode of coordination of the coordinated carbonate ligand. The first compound was suggested to have only bidentate coordination, which is in agreement with the solid-state structure. However, 2, 4 and 5 were suggested to have both mono- and bidentate carbonato ligands; this assignment is incorrect for compound 4 for which an X-ray structure is available. This review concludes that the assignment of ligand bonding mode based on IR data should be made with caution.

[1969NOR]

The author has used liquid-liquid extraction with thenoyltrifluoroacetone (TTA) and potentiometry using a fluoride selective electrode to determine the stoichiometry and equilibrium constants of the fluoride complexes of Th(IV) and U(IV); only the Th(IV) data will be discussed here as the U(IV) data have been reviewed previously in [1992GRE/FUG]. The experiments have been made in a 4 M $HClO_4$ ionic medium at 20°C. The experimental data are described in detail and this study provides very useful information on the quality of the two experimental approaches used. The same author has previously studied the Zr(IV) and Hf(IV) systems using the same experimental approach. The slope of the ion selective electrode was determined experimentally and equilibrium was assumed to be attained when the emf changed by less than 0.1 mV/h. The experiments were made at three different total concentrations of Th(IV), 0.90, 1.79 and 4.48 mM and with the total concentration of HF varying from 0.406 to 225 mM. This corresponds to a concentration of free fluoride, $8\times10^{-8} < [F^-] < 5\times10^{-3}$ M. The analysis of the experimental emf data is straightforward and the conditional equilibrium constants for the two reactions:

$$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$$
$$({}^*K_1 = (1.19 \pm 0.01)\times10^4\ M^{-1} \quad {}^*\beta_1 = (4.76 \pm 0.04)\times10^4)$$

$$Th^{4+} + 2HF(aq) \rightleftharpoons ThF_2^{2+} + 2H^+$$
$$({}^*K_2 = (2.8 \pm 0.1)\times10^6\ M^{-2} \quad {}^*\beta_2 = (4.48 \pm 0.16)\times10^7)$$

are accepted by this review, but the uncertainty of ${}^*K_1$ has been increased by a factor of 5. The conditional constants ${}^*K_n$ include the factor $[H^+]^n$, *i.e.:*

$${}^*K_n = [ThF_n^{4-n}]/([Th^{4+}][HF(aq)]^n) \text{ and hence } {}^*K_n [H^+]^n = {}^*\beta_n$$

where ${}^*\beta_n$ are the true equilibrium constants for the reactions above. Note that Norén has used the opposite notation.

The liquid-liquid extraction study has been made using a total concentration of Th(IV) equal to 0.1 mM and with the total concentration of HF varying from 0 to 0.961 mM, so that only the equilibrium constant for the formation of ThF^{3+} can be determined from these data. The reason is the low extraction of Th(IV) at the very high hydrogen concentration used, even at the very high concentration of TTA = 1.98 M in the benzene phase. The equilibrium constant thus determined, ${}^{*}K_1 = (1.1 \pm 0.1) \times 10^4$ M^{-1}, and ${}^{*}\beta_1 = (4.4 \pm 0.1) \times 10^4$, is in fair agreement with the potentiometric value, but less precise.

The true equilibrium constants for the reactions above, ${}^{*}\beta_1 = (4.76 \pm 0.20) \times 10^4$ and ${}^{*}\beta_2 = (4.48 \pm 0.16) \times 10^7$, are accepted by this review and included in the evaluation of the selected values.

[1969SMI/THA]

The following enthalpies of solution of Th(cr), $ThCl_4$ (cr), U(cr), UCl_4(cr) in HCl were obtained at 298.15 K: Th(cr): $-(761.1 \pm 0.8)$ kJ·mol^{-1} and $ThCl_4$(cr): $-(186.8 \pm 0.8)$ kJ·mol^{-1}, in 6.06 M HCl - 0.005 M Na_2SiF_6; U(cr): $-(605.8 \pm 5.2)$ kJ·mol^{-1} and UCl_4(cr): $-(168.9 \pm 3.0)$ kJ·mol^{-1} in 6.03 M HCl - 0.005M Na_2SiF_6. The concentrations of thorium and uranium in the solutions were in the 1 to 3 millimolar range.

The results reported by these authors for the enthalpy of solution of Th(cr) and $ThCl_4$(cr) agree well with other literature values. Although little information is given in this paper on the characterisation of the compounds, these data are used, in conjunction with the enthalpy of solution of the metal and of the tetrachloride in 6.00 M HCl - 0.005 M Na_2SiF_6 [1950EYR/WES], and of the tetrachloride in 6.00 M HCl [1973FUG/BRO], to evaluate $\Delta_f H_m^\circ$ (Th^{4+}) and $\Delta_f H_m^\circ$ ($ThCl_4$, β).

[1969ZMB]

This paper reports a mass-spectrometric study of the reactions between Ca(g) and ThF_4(g) over the temperature range 1308 to 1336 K. In addition to these species, CaF^+, ThF_2^{2+} and ThF_3^+ were observed in the mass spectrum arising from a mixture of CaF_2(cr) and Th(cr) heated in a molybdenum effusion cell. “Equilibrium” constants were calculated for the two reactions $Ca(g) + nThF_4(g) \rightleftharpoons ThF_{4-n}(g) + nCaF(g)$, $n = 1, 2$, assuming the required corrections for ionisation cross-sections and instrumental sensitivities cancel for such reactions. Third-law enthalpies of reactions were calculated assuming constant values of $\Delta_r(G_m(T) - H_m(298.15\text{ K}))$ over the short temperature range, based on values for the similar reactions involving zirconium. No second-law values were reported, owing to the very short temperature range of the study.

These data are a subset of those reported in [1970ZMB] and it should be noted that the headings of Table 3 in [1969ZMB] are incorrect – the equilibrium constants reported as K_1 and K_2 are in fact values of $10^3 \cdot K_1$ and $10^4 \cdot K_2$, as in [1970ZMB]. This is clear from the reported values of $\Delta_r(G_m(T) - H_m(298.15\text{ K}))$ and $\Delta_r H_m(298.15\text{ K})$.

These data are discussed in Section VIII.1.1.1.2.

[1970BAU]

A lanthanum fluoride membrane electrode was used to measure free fluoride concentrations in test solutions that contain mixtures of NaF, HF or HNO_3 and $Th(NO_3)_4$ in

0.01 M NH_4NO_3 with the total ionic strength maintained at (0.01 ± 0.001) M. The experiments are described in detail, and the response of the fluoride electrode in different solutions and at different temperatures is discussed. Thorium fluoride equilibrium data (free fluoride molar concentrations and total molar concentrations of fluoride, hydrogen, and thorium) at 5, 25, and 45°C are presented in tabular form.

The experimental data are interpreted through the average number of fluorides per thorium atom. The concentration-dependent stability constants thus calculated were converted to constants at zero ionic strength through the modified Debye-Hückel relationship for the experimental temperatures. These constants were then used to calculate other thermodynamic parameters through the use of van't Hoff relationship assuming that $\Delta_r H^\circ_m$ (A.60) is independent of temperature. The $\log_{10} K_n$ (A.60) values for:

$$\mathrm{ThF}_{n-1}^{(5-n)+} + \mathrm{F}^- \rightleftharpoons \mathrm{ThF}_n^{(4-n)+} \qquad \text{(A.60)}$$

at different temperatures, 0.01 M ionic strength, and at zero ionic strength reported by the authors are shown in Table A-34.

Table A-34: Equilibrium constants for the stepwise Reactions (A.60).

Equilibrium constant	Experimental temperatures		
	5°C	25°C	45°C
	0.01 M NH_4NO_3		
$\log_{10} K_1$	8.11	8.08	7.95
$\log_{10} K_2$	6.29	6.36	6.20
$\log_{10} K_3$	4.64	4.57	4.55
$\log_{10} K_4$	3.33	3.28	3.71[a]
	Zero ionic strength		
$\log_{10} K_1^\circ$	8.46	8.44	8.32
$\log_{10} K_2^\circ$	6.55	6.62	6.48
$\log_{10} K_3^\circ$	4.81	4.75	4.73
$\log_{10} K_4^\circ$	3.41	3.36	3.80[a]

a: The author considers these value as dubious.

The values of equilibrium constants for ThF_n^{4-n}, with n varying from 1 to 4, at zero ionic strength reported by [1970BAU] are in all cases lower than the values reported by many other authors (*e.g.*, [1951ZEB/ALT], [1950DAY/STO], [1949DOD/ROL], [1990SAW/CHA2], see Table VIII-6 for details), indicating a systematic error in the data reported by [1970BAU]. The equilibrium constant for the formation of $ThF_4(aq)$ reported by [1970BAU] is unreliable due to suspected precipitation of ThF_4(cr, hyd) at the higher fluoride concentrations used in the experiments. Therefore, this review has not accepted the values reported by [1970BAU]. This review has also not accepted the enthalpies and entropies of the reaction proposed by [1970BAU] because of uncertainties in the quality of equilibrium data and the limited temperature range used to determine the enthalpies of reaction. Although the equilibrium data reported by [1970BAU] are not accepted in this review, it is of interest to determine how well the NONLINT-SIT predicted concentrations based on the equilibrium data recommended in this review (Tables VIII-6 and VIII-7) compare with the experimental data reported by [1970BAU]. The experimental and predicted F^- activities are compared in Figure A-24 and the distribution of different predicted species is listed in Table A-35. These comparisons (Figure A-24 and Table A-35) between the predicted and experimental F^- activities show a close agreement (but systematically too low) at relatively high fluoride concentrations ($\log_{10}[F^-] > -6.5$) and up to about 0.5 log-units lower experimental activities than the predicted at relatively low fluoride concentrations ($\log_{10}[F^-] < -6.5$).

Figure A-24: Observed ([1970BAU]) and predicted F^- activities at 25°C for fluoride-selective electrode studies in 0.01 M NH_4NO_3 solutions. Predictions based on NONLINT-SIT calculations using the thermodynamic data summarised in Tables VIII-8 and VIII-9.

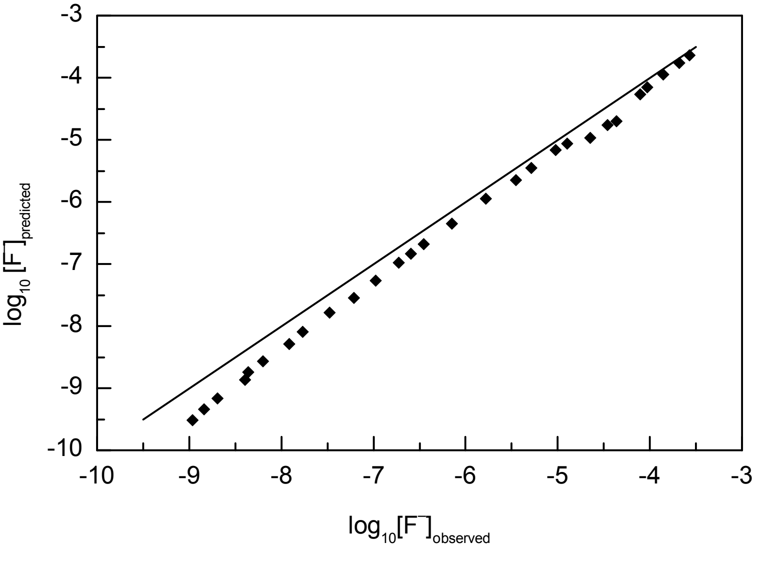


Table A-35: Experimental [1970BAU] and predicted concentrations at 25°C for fluoride-selective electrode data.

Experimental concentrations (m)						Predicted concentrations (m)[a]						
H_{Total}	NH_4	NO_3	Th_{Total}	F_{Total}	$F^-_{activity}$	$F^-_{activity}$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	$ThF_4(aq)$	ThF_6^{2-}
8.038E-04	5.438E-03	7.707E-03	3.758E-04	3.778E-05	1.090E-09	3.055E-10	3.381E-04	3.770E-05	3.997E-08	9.899E-13	7.000E-14	7.000E-14
8.426E-04	6.400E-03	8.306E-03	2.757E-04	3.960E-05	1.450E-09	4.571E-10	2.362E-04	3.947E-05	6.272E-08	2.328E-12	7.000E-14	7.000E-14
8.705E-04	7.059E-03	8.738E-03	2.035E-04	4.092E-05	2.030E-09	6.839E-10	1.627E-04	4.072E-05	9.690E-08	5.386E-12	7.000E-14	7.000E-14
9.004E-04	7.837E-03	9.200E-03	1.263E-04	4.232E-05	4.020E-09	1.361E-09	8.418E-05	4.192E-05	1.984E-07	2.195E-11	7.000E-14	7.000E-14
9.082E-04	8.030E-03	9.320E-03	1.062E-04	4.269E-05	4.400E-09	1.807E-09	6.378E-05	4.216E-05	2.649E-07	3.889E-11	7.000E-14	7.000E-14
9.162E-04	8.227E-03	9.443E-03	8.566E-05	4.306E-05	6.300E-09	2.685E-09	4.300E-05	4.226E-05	3.949E-07	8.620E-11	7.000E-14	7.000E-14
9.242E-04	8.428E-03	9.568E-03	6.481E-05	4.344E-05	1.220E-08	5.176E-09	2.214E-05	4.192E-05	7.545E-07	3.173E-10	1.217E-13	7.000E-14
9.275E-04	8.509E-03	9.618E-03	5.637E-05	4.359E-05	1.700E-08	8.091E-09	1.396E-05	4.125E-05	1.159E-06	7.606E-10	4.553E-13	7.000E-14
9.308E-04	8.591E-03	9.669E-03	4.787E-05	4.374E-05	3.340E-08	1.663E-08	6.440E-06	3.916E-05	2.264E-06	3.058E-09	3.768E-12	7.000E-14
9.324E-04	8.632E-03	9.695E-03	4.359E-05	4.383E-05	6.090E-08	2.864E-08	3.479E-06	3.647E-05	3.634E-06	8.460E-09	1.797E-11	7.000E-14
9.341E-04	8.673E-03	9.720E-03	3.930E-05	4.390E-05	1.050E-07	5.458E-08	1.589E-06	3.168E-05	6.005E-06	2.660E-08	1.074E-10	7.000E-14
9.358E-04	8.714E-03	9.746E-03	3.500E-05	4.398E-05	1.875E-07	1.059E-07	6.478E-07	2.506E-05	9.215E-06	7.918E-08	6.206E-10	7.000E-14
9.366E-04	8.735E-03	9.759E-03	3.284E-05	4.402E-05	2.560E-07	1.476E-07	3.958E-07	2.136E-05	1.096E-05	1.313E-07	1.436E-09	7.000E-14
9.374E-04	8.756E-03	9.772E-03	3.068E-05	4.406E-05	3.510E-07	2.080E-07	2.311E-07	1.755E-05	1.268E-05	2.139E-07	3.292E-09	7.000E-14
9.391E-04	8.798E-03	9.798E-03	2.634E-05	4.414E-05	7.100E-07	4.457E-07	6.194E-08	1.008E-05	1.561E-05	5.647E-07	1.863E-08	7.000E-14
9.408E-04	8.839E-03	9.824E-03	2.199E-05	4.421E-05	1.666E-06	1.122E-06	1.015E-08	4.160E-06	1.622E-05	1.478E-06	1.229E-07	7.000E-14
5.000E-04	9.377E-03	9.896E-03	1.235E-05	2.984E-05	3.502E-06	2.265E-06	1.417E-09	1.171E-06	9.203E-06	1.692E-06	2.838E-07	7.000E-14
2.007E-05	9.907E-03	9.937E-03	7.220E-06	2.018E-05	5.200E-06	3.516E-06	3.214E-10	4.114E-07	5.010E-06	1.427E-06	3.712E-07	7.000E-14
2.080E-05	9.931E-03	9.951E-03	4.820E-06	2.020E-05	9.500E-06	6.871E-06	4.303E-11	1.076E-07	2.561E-06	1.426E-06	7.250E-07	2.266E-13
5.030E-04	9.374E-03	9.877E-03	1.230E-05	4.921E-05	1.260E-05	8.770E-06	5.722E-11	1.831E-07	5.574E-06	3.967E-06	2.576E-06	1.311E-12
1.465E-04	9.532E-03	9.701E-03	3.217E-05	1.062E-04	2.260E-05	1.079E-05	8.319E-11	3.290E-07	1.236E-05	1.083E-05	8.654E-06	6.635E-12
1.649E-04	9.514E-03	9.682E-03	3.211E-05	1.249E-04	3.450E-05	1.722E-05	2.017E-11	1.274E-07	7.641E-06	1.070E-05	1.364E-05	2.665E-11
1.805E-04	9.350E-03	9.538E-03	4.697E-05	1.805E-04	4.350E-05	1.991E-05	1.823E-11	1.339E-07	9.324E-06	1.514E-05	2.237E-05	5.842E-11
1.582E-04	9.608E-03	9.701E-03	2.340E-05	1.582E-04	7.799E-05	5.433E-05	2.671E-13	5.322E-09	1.007E-06	4.452E-06	1.794E-05	3.501E-10
1.823E-04	9.581E-03	9.675E-03	2.372E-05	1.823E-04	9.380E-05	6.934E-05	1.084E-13	2.756E-09	6.657E-07	3.754E-06	1.930E-05	6.129E-10
4.754E-04	9.291E-03	9.580E-03	2.334E-05	2.801E-04	1.400E-04	1.138E-04	7.000E-14	6.687E-10	2.649E-07	2.449E-06	2.062E-05	1.756E-09
4.361E-04	9.252E-03	9.416E-03	3.122E-05	3.970E-04	2.100E-04	1.730E-04	7.000E-14	2.641E-10	1.595E-07	2.247E-06	2.881E-05	5.670E-09
9.886E-05	9.406E-03	9.498E-03	2.291E-05	3.649E-04	2.672E-04	2.275E-04	7.000E-14	8.697E-11	6.906E-08	1.279E-06	2.155E-05	7.335E-09

a: All 7.000E-14 numbers are model limiting values, the actual value is lower than this.

[1970DEV/RUD]

The energy of formation of ThF_4(cr) was measured by combination of the elements in a bomb calorimeter. Five samples (*ca.* 2 g) of thorium foil, in which the principal impurities were 520 ppm O, 225 ppm C and 200 ppm Fe, were combusted in 25 atm fluorine. The small residues (0.7 to 1.8%) of unburnt thorium were determined by dissolution of the product in 50% HCl containing 5% H_2SiF_6 and measuring the hydrogen evolved. The product was identified to be ThF_4(cr) from its monoclinic X-ray pattern. The derived enthalpy of formation was $\Delta_f H_m$ (ThF_4, cr, 298.15 K) = – (2110.8 ± 5.0) $kJ\cdot mol^{-1}$.

[1970NOV/COS]

This paper deals principally with the electronic structure of $UC_{1-x}N_x$ solid solutions, but for comparative purposes, de Novion and Costa measured the magnetic susceptibility of ThN(cr) from 3.5 to 8.9 K, from which the coefficient γ of the electronic contribution to the heat capacity C_v(electronic) = γT was found to be 3.12 $mJ\cdot K^{-2}\cdot mol^{-1}$. This value was used by Adachi *et al.* [2005ADA/KUR] as supplementary information in their calculations of the heat capacity of ThN(cr).

[1970SER/ALM]

This is a potentiometric study made at 25°C and an ionic strength of 0.50 M. The total concentration of thorium varied from 5 to 0.25 mM and the value of $\bar{n}_{OH}$ from 0.01 to 2.58. The authors demonstrate the formation of polynuclear complex but they have preferred to analyse their data using the "core and link" model described in [1964HIE/SIL]. The experimental data are consistent with this model, but as this does not provide a proper chemical description of the constitution of the complexes, as discussed in the present review, these data are not accepted by this review.

[1970ZMB]

This journal paper reports briefly the 'equilibrium' constants for the reactions between Ca(g) and ThF_4(g), many of which were also reported in the conference paper [1969ZMB], *q.v.* However, [1970ZMB] reports additional measurements, extending the temperature range of the study from 1288 to 1341 K, and also reports the correct orders of magnitude of the calculated constants for the two reactions Ca(g) + $n$$ThF_4$(g) $\rightleftharpoons$ ThF_{4-n}(g) + nCaF(g), n = 1, 2.

These data are discussed in Section VIII.1.1.1.2.

[1971BRE]

The thermodynamic data for the lanthanide and actinide metals were combined with spectroscopic data to develop a method of estimating the energies of the electronic configurations of the neutral gaseous atoms. Energies are tabulated for the lowest spectroscopic level of each configuration. In particular for Th(g), there are seven such levels not identified in the current (1992) listing [1992BLA/WYA] These are estimated to lie at 20000, 23000, 28000, 31000, 39000(2) and 42000 cm^{-1}, so they will not contribute to the thermal functions of Th(g) to any significant extent at temperatures relevant for the review, but they have nevertheless been included in the calculations for completeness.

[1971HEI/DJE]

This is a study of the reduction of thoria by carbon from 2156 to 2410 K. The results indicated that 1.96, rather than 2, mole of CO(g) were formed per mole of thorium, suggesting the probable dissolution of some oxygen in the dicarbide. The equilibrium pressure of CO(g) was given by the expression $\log_{10} p_{\mathrm{CO}}/\mathrm{bar} = 9.57 - 2.335\times10^{4}\,T^{-1}$ in the temperature range studies. These data are included in the discussion of $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{ThC_2}$, cr) in Section XI.1.1.3.

[1971KIC/STE]

Kiciak and Stefanowicz performed potentiometric measurements at an approximately constant low thorium concentration of $[\mathrm{Th}]_{\mathrm{tot}}$ = 0.68 – 0.76 mM and low ionic strength (I = 0.01 – 0.04 M) at 20°C. The titrant was 0.100 M NaOH, no ionic medium was used. The ionic strength is given by the sum of the initial $\mathrm{Th(NO_3)_4}$ and acid concentrations ($\mathrm{HNO_3}$, HCl or $\mathrm{HClO_4}$) and varied throughout the titrations up to pH 4.5, typically from 0.016 to 0.011 M and 0.023 to 0.016 M.

A precision pH-meter (accuracy of 0.005 pH units) and a glass and calomel reference electrode calibrated against pH standards were used to measure pH values (activity units) which were converted into $-\log_{10}[\mathrm{H}^+]$ using the Debye-Hückel equation. However, the absolute accuracy that can be achieved with the applied electrode calibration is at best ±0.02 pH-units, which is not sufficient for the determination of accurate results from potentiometric titration data. This problem becomes evident from the results shown in Table 1 of [1971KIC/STE]. The value of $\bar{n}_{\mathrm{OH}}$ = 0.5 was reached at pH = (3.00 ± 0.05) in titrations starting at initial acid concentrations below 0.01 M (I = 0.013 − 0.016 M) and at pH = (3.40 ± 0.05) in titrations starting at initial acid concentrations of about 0.03 M (I = 0.037 M).

The authors assumed that polynuclear complexes can be neglected under their experimental conditions and calculated the following equilibrium constants $\log_{10} {}^{*}\beta_{n,1}$ ($\mathrm{Th(OH)}_n^{4-n}$), (mean values at I = 0.01 − 0.04 M), for the mononuclear Th(IV) hydroxide complexes:

$$\log_{10} {}^{*}\beta_{1,1} = -(3.61 \pm 0.20)$$

$$\log_{10} {}^{*}\beta_{2,1} = -(7.62 \pm 0.20)$$

$$\log_{10} {}^{*}\beta_{3,1} = -(11.17 \pm 0.20)$$

$$\log_{10} {}^{*}\beta_{4,1} = -(14.43 \pm 0.20).$$

In the review of Baes and Mesmer [1976BAE/MES], the equilibrium constants for $\mathrm{Th(OH)}^{3+}$ and $\mathrm{Th(OH)}_2^{2+}$ were designated as “useful estimates” but it was remarked that the equilibrium constant for $\mathrm{Th(OH)_2^{2+}}$ might possibly be affected by the interference of the dinuclear species $\mathrm{Th_2(OH)_2^{6+}}$. The slight variation of ionic strength has no dramatic effect on the extrapolation to zero ionic strength: $\log_{10} {}^*\beta^{\circ}_{1,1} = -3.2$ and $\log_{10} {}^*\beta^{\circ}_{2,1} = -7.0$. However, for the experimental reasons discussed above, these equilibrium constants should also be used with caution. The equilibrium constants for $\mathrm{Th(OH)_3^{+}}$ and particularly for $\mathrm{Th(OH)_4(aq)}$, which is calculated to be the predominant complex at pH 3.5−4.5 according to Figure 3 in [1971KIC/STE], are not reliable. It is well known from other potentiometric titration studies that polynuclear complexes with high positive charge are predominant under these conditions (pH range, thorium concentration), also at low ionic strength (*cf.* [1983BRO/ELL]).

It is obvious from the introduction that the authors were not aware of the current literature at the time, a fact that might explain both their neglect of polynuclear complexes and the far from adequate calculation method used to calculate the equilibrium constants from the experimental $\bar{n}_{\mathrm{OH}}$ *vs.* pH data. The reported equilibrium constants are not reliable because of an erroneous chemical model, the neglect of polynuclear species that are totally dominating the speciation under the experimental conditions used.

[1971KLO/MUK]

In this study of thorium fluoride complexes, the experimental method is the same as used in [1969NOR] but the experiments have been made at 25°C and two different constant total concentrations of $\mathrm{H^+}$, 0.100 and 1.00 M. The ionic strength was 3.00 M using $\mathrm{(Na,H)ClO_4}$ as the ionic medium. Titrations were made at three different total concentrations of Th(IV), 3, 10 and 30 mM. Precipitation of $\mathrm{ThF_4(s)}$ took place when $\bar{n}_{\mathrm{F}}$ was slightly below 2, but the titrations were continued in the presence of the solid. These experiments indicated that the initial solid phase was transformed to $\mathrm{NaThF_5(s)}$. Analysis of the experimental resulted in the following equilibrium constants: $\log_{10} {}^*\beta_1 = (4.52 \pm 0.05)$; $\log_{10} {}^*\beta_2 = (7.26 \pm 0.14)$; $\log_{10} {}^*\beta_3 = (8.9 \pm 0.3)$. The solubility constant for the reaction:

$$\mathrm{ThF_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq)}; \qquad \log_{10} {}^*K_{s,0} = -(15.17 \pm 0.15).$$

By using the dissociation constant for HF(aq) with $\log_{10} K_{\mathrm{HF}} = 3.28$, valid in 3.00 M $\mathrm{NaClO_4}$ they obtain: $\log_{10} \beta_1 = (7.80 \pm 0.05)$; $\log_{10} \beta_2 = (13.82 \pm 0.14)$; $\log_{10} \beta_3 = (18.8 \pm 0.3)$ and $\log_{10} K_{s,0} = -(28.29 \pm 0.15)$.

This is a precise study with all necessary information required to assess the methodology used and the equilibrium constants and their estimated uncertainty are accepted by this review.

[1971KOR/DRO]

The equilibrium constant for the reaction $\mathrm{ThCl_4(cr) + 0.5O_2(g) \rightleftharpoons ThOCl_2(cr) + Cl_2(g)}$ at six temperatures from 743 to 895 K is given by $\log_{10} K_p/\mathrm{bar}^{0.5} = -636/T - 0.458$, corresponding to an enthalpy of reaction of (12.1 ± 4.2) kJ·mol^{-1} at 820 K. The equilibrium was approached from the oxygen-rich side, since the reaction between $ThOCl_2$(cr) and chlorine was extremely slow.

As noted in Section VIII.2.1.6.1, these data are discounted, since the derived enthalpy of formation of $ThOCl_2$(cr) does not agree with other consistent determinations, and the calculated entropy of reaction is negative, which is unlikely for a reaction in which a net 0.5 mole of gas is formed. It seems likely that equilibrium was not reached in these experiments, or the presence of adventitious water affected the results.

[1971KUS/IMO]

Th_3N_4(cr) and Th_2N_2O(cr) were thermally decomposed at 1473 − 1623 K in vacuum. In both cases, the lattice parameter of ThN(cr) produced by the decomposition varied from 5.156 to 5.161 Å, in good agreement with those previously reported, when the decomposition was nearly completed; but, when the product contained a large amount of the undecomposed Th_3N_4 or Th_2N_2O phase, a value as high as 5.180 Å was observed. The equilibrium nitrogen pressures for the reactions:

$$2Th_3N_4(cr) \rightleftharpoons 6ThN(cr) + N_2(g)$$

$$4Th_2N_2O\ (cr) \rightleftharpoons 6ThN(cr) + 2ThO_2(cr) + N_2(g)$$

(the reaction assumed by this review) were determined by heating the specimen in a disk form on a W strip heater up to 2258 K under predetermined N_2 pressures and measuring the decomposition temperature from the change of the specific emissivity at that point. The results are: $\log_{10} p_{N_2}/\text{bar} = 6.215 - 1.399\times10^4/T$ for $Th_3N_4(cr) \rightleftharpoons ThN(cr)$, $\log_{10} p_{N_2}/\text{bar} = 13.550 - 3.095\times10^4/T$ for $Th_2N_2O(cr) \rightleftharpoons ThN(cr) + ThO_2(cr)$. These data are discussed in Sections X.1.1.1 and X.1.1.4.

[1971LAU/FOU]

Laubscher and Fouché studied the formation of Zr(IV), Hf(IV) and Th(IV) thiocyanate complexes by liquid-liquid extraction.

Only the Th(IV) data will be discussed here. The equilibrium constants have been determined in a 3.00 M $(Na^+,H^+)\,ClO_4^-$ ionic medium with a constant hydrogen ion concentration of 0.500 M. There is no information about the temperature and this review has assumed that they refer to 25°C. The equilibrium analysis 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 $0.00\text{ M} < [SCN^-] < 1.00\text{ M}$ in the TTA system and $0.00\text{ M} < [SCN^-] < 2.50\text{ M}$ in the DNNS system, respectively. The equilibrium constants deduced from these data are given in Table A-36; this table also includes data from [1950WAG/STO].

Table A-36: Equilibrium constants determined in a 3.00 and 1.00 M $(Na^+,H^+)ClO_4^-$ ionic medium reported in [1971LAU/FOU] and [1950WAG/STO], respectively.

Method	Ionic medium $[H^+] = 0.50$ M	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})	Reference
DNNS	$I = 3.00$	7.12 ± 1.11	33.9 ± 5.3	14.3 ± 7.3	32.4 ± 2.7	[1971LAU/FOU]
TTA	$I = 3.00$	9.01 ± 0.62	25.1 ± 2.7	5.8 ± 2.6	-	[1971LAU/FOU]
TTA	$I = 1.00$	12.1	60	-	-	[1950WAG/STO]

The results reported by Waggener and Stoughton [1950WAG/STO] were given without any details in an ORNL quarterly report. The values of β_1 and β_2 are in fair agreement in 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 ClO_4^- 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 artefacts due to the activity factor variations resulting from the changes in the ionic medium. This review has only accepted the values of β_1 and β_2 and selected their average and an uncertainty range that covers their respective uncertainties, $\beta_1 = (8.0 \pm 1.5)\ M^{-1}$, $\beta_2 = (30 \pm 10)\ M^{-2}$, $\log_{10}\beta_1 = (0.90 \pm 0.08)$ and $\log_{10}\beta_2 = (1.48 \pm 0.14)$. These values differ significantly from those proposed in the Raman study of Manouvrier and Devaure [1978MAN/DEV].

[1971LOR/DIE]

These authors measured the enthalpies of combustion of thorium and plutonium carbides by oxygen bomb combustion calorimetry.

Samples of various stoichiometries were prepared by sintering mixtures of the hydrides and graphite in the appropriate ratios under vacuum (*ca.* 10^{-8} bar) at 1673 K. Determination of carbon (combustion), oxygen and nitrogen (reducing fusion under He), as well as phase analysis (X-ray diffraction and metallography) are mentioned, but no details were given. Elementary analysis indicated metallic impurities in amounts smaller than 300 parts per million.

In the case of the thorium carbides, three to eight combustion experiments were carried out for each sample. The reported combustion yields ranged between 90 and 100%.

The reported enthalpies of formation in $kJ\cdot mol^{-1}$ at 298.15 K are given in Table A-37.

Table A-37: Enthalpy of formation of ThC_x(cr).

x = C/Th	$-\Delta_f H_m^o$ (ThC_x, cr) (kJ·mol^{-1})	Number of measurements
0.76	36.0 ± 7.1	6
0.80	59.4 ± 7.9	3
0.84	69.3 ± 12.6	5
0.85	69.5 ± 5.0	4
0.95	118.4 ± 6.3	6
0.96	97.5 ± 14.6	8
1.01	126.4 ± 10.5	7
1.20	141.4 ± 8.4	5
1.91	159.0 ± 16.7	5

[1971MIL2]

Milić and other members of the Sillén group have made extensive studies of the hydrolysis of Th(IV) in a number of different ionic media. The experimental methods are the same in all of these studies and will not be commented upon; it is sufficient to note that they represent the state of the art in potentiometric investigations. The present study includes a large number of titrations and all experimental data are reported in the paper. The study covers a $[Th]_{tot}$ range from about 1 mM to 120 mM and a $-\log_{10}[H^+]$ range from 2 to about 3.5. The values of $\bar{n}_{OH}$ are at most 0.6 in these studies and the concentration of the (15,6) complex is therefore not as large as in the perchlorate ionic media. This may also be the reason why the (8,4) complex was not identified. The analysis of the data was made using the least-squares method LETAGROP, often with additional analysis of systematic errors. The initial analysis of the average number of hydroxide per thorium and the nuclearity was made using the graphical methods of Sillén and the final analysis using least-squares fitting. The selected set of "best-fitting" complexes and their equilibrium constants are given in Table A-38.

The agreement between calculated and experimental data is excellent with these constants. From the SIT we expect that the equilibrium constant for a certain cationic complex will not depend strongly on the cation in the ionic medium; this is also the case with the exception of the constant for the (15,6) complex. In view of the small amounts of this complex in the test solutions we suggest that the estimated uncertainty in the equilibrium constant is too small. The species $Th_3(OH)_5^{7+}$ is present in large amounts in the test solutions and represents a species not found in perchlorate media. As shown by Baes and Mesmer [1976BAE/MES], these data can as well be described with the model appropriate for $NaClO_4$ solutions, including the species (2,2), (8,4) and (15,6). Accordingly, the equilibrium constant for the (5,3) complex from [1971MIL2] has not been selected by this review. The complex $Th_2(OH)_3^{5+}$ is present in small amounts and we do not consider this species as definitively identified.

Table A-38: Equilibrium constants of Th(IV) hydroxide complexes formed in 3 M Li, K and Mg nitrate ionic media at a temperature of 25°C. The reported uncertainty is equal to 3σ. Constants without uncertainty estimates are not well determined and correspond to species that are present in small amounts in the test solutions, *cf.* Figs. 9 and 10 in [1971MIL2].

Ionic medium	Complex	$\log_{10}{}^{*}\beta_{n,m}$
3 M (Li)NO_3	$Th_2(OH)_2^{6+}$	– 5.14 ± 0.01
	$Th_3(OH)_5^{7+}$	– 14.23 ± 0.06
	$Th_3(OH)_3^{9+}$	max – 7.33
3 M (K)NO_3	$Th_2(OH)_2^{6+}$	– 5.10 ± 0.03
	$Th_2(OH)_3^{5+}$	– 8.98 ± 0.08
	$Th(OH)_2^{2+}$	– 9.67 max – 8.90
	$Th_6(OH)_{15}^{9+}$	– 40.95 ± 0.07
3 M (Mg)NO_3	$Th_2(OH)_2^{6+}$	– 5.17 ± 0.01
(= 1.5 M $Mg(NO_3)_2$)	$Th_3(OH)_5^{7+}$	– 14.29 ± 0.07
	$Th_6(OH)_{15}^{9+}$	– 43.20 ± 0.08

[1971SAS/KUB]

The Langmuir vaporisation and the surface ionisation of solid ThC_2 + C (and also LaC_2, CeC_2, PrC_2, NdC_2, and UC_2) from a heated graphite filament were studied mass spectrometrically from *ca.* 2545 to 2780 K (for ThC_2). Small amounts of neutral and ionic metal dicarbide were present in addition to neutral and ionic metal atoms in all the MC_2-C systems except for NdC_2-C. The enthalpy of the reaction $Th(g) + 2C(cr) \rightleftharpoons ThC_2(g)$ was calculated by the authors to be $\Delta_r H_m(2662\ K) = (108.0 \pm 19.7)\ kJ\cdot mol^{-1}$ from the slope of the neutral MC_2/M ratio, the uncertainty not including those relating to the detector efficiency and ionisation cross-sections of Th(g) and ThC_2(g).

[1971TAN/YAM]

The Gibbs energy of formation of ThF_4(cr) was determined at 873 K with emf cells using a CaF_2 solid electrolyte and Al/AlF_3, UF_3/UF_4 and U/UF_3 counter electrodes.

ThF_4 was prepared from a mixture of ThO_2(cr) and 20% excess NH_4HF_2 maintained at 433 K, followed by heating to 623−673 K in purified argon and removal of volatile material at 973 K. Reaction between ThF_4 and CaF_2 was minimised by using a single crystal of CaF_2 as the electrolyte.

Steady emf values were obtained, but no details are given in the translation available to the reviewers. Measurements were made only at 873 K. The data are analysed by the third-law in Section VIII.1.1.2.3.

[1971USH/SKO]

In this paper on the formation of acetate complexes of scandium and thorium in water and aqueous ethanol mixtures at I = 0.05 M and 25°C, Usherenko and Skorik [1971USH/SKO] used preliminary hydrolysis constants of $\log_{10} {}^{*}\beta_{1,1}$ ($\mathrm{Th(OH)}^{3+}$) = −3.15 (water, I = 0.05 M), −2.77 (25 vol.%/19.8 mass.% ethanol) and −2.17 (50 vol.%/40.3 mass% ethanol). The experimental determination of the hydrolysis constants is reported in a later paper of these authors [1972USH/SKO].

[1972ACK/RAU]

The vapour pressure of Th(l) was determined by a combination of target mass-effusion (2380 to 2494 K) and mass-spectrometric (2010 to 2460 K) techniques, using single crystal tungsten cup inside a tungsten effusion cell. Crystal-bar thorium of high (99.95%) purity was used, but no detailed analyses are given. Prior to the measurements of a given sample, it was placed in the mass-spectrometer source and heated until the ThO(g) intensities were less than 2% of the total metal intensity. This treatment was repeated after transfer to the effusion cell. The mass of thorium on the targets (*ca.* 1 µg) was determined by activation analysis. In the mass-spectrometric experiments the initial ThO^{+} intensity was *ca.* five times that of Th^{+}, but fell by a factor of 250 after 6 h treatment at 2400 K.

The melting point of Th was measured to be 2020 K, and the eutectic temperature with tungsten 1968 K. The solubility of W in Th(l) was found to be small, varying linearly from 1.5 mol% at 2000 K to 3.0 mol% at 2500 K. No correction was made for the small solubility of tungsten in Th(l). The absolute mass-loss effusion measurements were used to normalise the mass-spectrometric data, to give the vapour pressure equation for Th(l), $\log_{10} p_{\mathrm{Th}} / \mathrm{bar} = -(29770 \pm 220)/T + (6.030 \pm 0.098)$ from 2010 to 2460 K. The uncertainties are the authors' $1-\sigma$ values.

The vapour pressures of Hf(cr), Hf(l) and Zr(l) were also measured by the same techniques. For all three elements, the measured vapour pressures are consistent with the thermodynamic properties of the vapour and condensed phases.

[1972DAN/NOV]

The specific heat of ThN(cr) was measured at 7 to 300 K in an adiabatic calorimeter, with a claimed accuracy of 1% at low temperatures and 2.5% at 300 K. The ThN sample had a lattice parameter of (5.1591 ± 0.0003) Å and contained about 2000 ppm oxygen, which X-ray analysis indicated was present as 1.5 wt% $\mathrm{ThO_2}$. It is not clear whether the authors corrected their heat capacities for this. Only heat capacity values at round temperatures from 10 to 300 K are reported, together with S°_{m} (ThN, cr, 298.15 K) = (56.0 ± 1.5) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The value of $C^{\circ}_{p,\mathrm{m}}$ (ThN, cr, 298.15 K) interpolated from the reported values at 280 and 300 K is (45.0 ± 1.1) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

[1972KNA/MUL]

Mass-loss Knudsen effusion was used to determine pressures of $ThCl_4$(g) in the thermal decomposition reaction, $2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$, from 819 to 1006 K:

$$\log_{10} p_{ThCl_4}/\text{bar} = -14573/T - 3.27\log_{10} T + 21.36.$$

The results were processed by the review (Section VIII.2.1.6) by the second-law method to give the enthalpy of formation and standard entropy of the oxychloride. The oxychloride is appreciably more stable with respect to ThO_2(cr) and $ThCl_4$(cr) than is $ThOF_2$(cr) with respect to the similar reaction.

[1972KNA/MUL2]

The Knudsen effusion method was used to determine the vapour pressure of tetragonal $ThCl_4$ at 671 to 882 K. The melting point of $ThCl_4$ was also determined by DTA to be 1042.7 K.

$ThCl_4$ was prepared by chlorinating the residue from heating hydrated $Th(NO_3)_4$ in a graphite crucible with a mixture of Cl_2, CCl_4 and Ar at 1033 − 1059 K, and collecting the product in a quartz condenser at 573 − 673 K, to avoid organic contaminants. The product was stated to contain 99.6 − 100% $ThCl_4$, and left a residue of 0.1 − 0.5% ThO_2 after sublimation from the Knudsen cell.

The X-ray examination showed a tetragonal structure and the material was presumably the tetragonal β-modification normally found in such preparations. Mass-loss effusion measurements were made from a platinum Knudsen cell from 671 to 982 K, with good reproducibility. It was observed that a sample of $ThCl_4$ contaminated with water gave appreciably lower vapour pressures, between those for the anhydrous $ThCl_4$ and the decomposition pressure of $ThOCl_2$ (see [1972KNA/MUL]).

The vapour pressures were well represented by the equation:

$$\log_{10} p/\text{bar} = -11740/T - 3.273\log_{10} T + 20.165.$$

The entropy and enthalpy of sublimation were extrapolated by the authors to 298.15 K, but these values will depend on the values taken for the heat capacities of the solid and gas.

[1972KUS/IMO]

This is an English language version of [1971KUS/IMO].

[1972PAT/RAM]

An organic phase containing 0.05 M dinonyl naphthalene sulphonic acid in benzene was used to extract thorium from 2.0 M perchloric and sulphuric acid solutions at 10, 25, or 40°C. The data on K_d values as a function of temperature and molarity of HSO_4^- are presented. The authors report the values of equilibrium constants as a function of temperature and based on these values at 25°C, they have also reported values for heats and entropies of different reactions (listed in Table A-39).

Table A-39: Equilibrium constants (molal scale) as a function of temperature and enthalpies and entropies of reaction at 25°C; all values at $I_m = 2.204$ m.

Reaction	$\log_{10}{}^*\beta_n$ (at $I_m = 2.204$ m)		
	10°C	25°C	40°C
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	2.34 ± 0.07	2.26 ± 0.03	2.24 ± 0.13
$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+$	3.59 ± 0.01	3.56 ± 0.06	3.51 ± 0.03
	$\Delta_r H_m$ (kJ·mol^{-1})		$\Delta_r S_m$ (J·K^{-1}·mol^{-1})
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	– 3.8		31.0
$ThSO_4^{2+} + HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + H^+$	0		24.7

This review calculated the values of $\log_{10}{}^*\beta_n^\circ$ from the $\log_{10}{}^*\beta_n$ reported by [1972PAT/RAM] at different temperatures form the relationship:

$$\log_{10}{}^*\beta_n^\circ = (\log_{10}{}^*\beta_n - \Delta z^2 D + \Delta\varepsilon I_m) \pm (\sigma\Delta\varepsilon I_m)$$

using the SIT model. An appropriate temperature dependent value of D, the Debye-Hückel term, and ion interaction parameters ($\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$, $\varepsilon(H^+, ClO_4^-) \approx \varepsilon(H^+, HSO_4^-) = (0.14 \pm 0.02)$, and $\varepsilon(ThSO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1}) were used in these calculations (for details about the selection of these parameters see Section IX.1.3.2). The $\log_{10}{}^*\beta_1^\circ$ and $\log_{10}{}^*\beta_2^\circ$ values thus determined are (4.21 ± 0.32) and (5.71 ± 0.25) at 10°C, (4.19 ± 0.32) and (5.76 ± 0.25) at 25°C, and (4.26 ± 0.32) and (5.82 ± 0.25) at 40°C. The values at 25°C are very similar to the values calculated from several other sources (*e.g.*, [1958MAI/FOM], [1951ZEB/ALT], [1959ZIE]) and were used in deriving the final value selected in this review for these reactions. Table A-40 shows that there is close agreement between the experimental aqueous thorium concentrations at different sulphate concentrations and the concentrations predicted by the aqueous phase model selected in this review (Tables IX-2 and IX-5). The aqueous thorium concentrations are not reported in this paper but were calculated from the reported K_d values assuming that the concentration $[Th_{org}]$ is constant at 10^{-6} m. Graphical comparisons are presented in Figure IX-4 (See Section IX.1.3.2).

[1972PER]

The author has studied the hydrolysis of Th(IV) by dilution of 3.56 mM thorium nitrate solutions at pH 3.1−3.8 with dilute HNO_3 solutions of the same pH and of 0.393 M thorium nitrate solutions at pH 2.92 with solutions of pH 2.0−2.7 and measuring the resulting change in pH. The method will in principle provide some information on hydrolysis, but data of this type require much more experimental work than the "standard" titration methods. Quantitative evaluation requires that the ionic medium is constant and this is not the case here. There is no quantitative evaluation of the experimental data and the conclusions are only qualitative and provide no thermodynamic information.

Table A-40: Observed [1972PAT/RAM] and predicted aqueous thorium concentrations at 25°C for solvent extraction studies from 2.2 m $HClO_4$-H_2SO_4 (data are plotted in Figure IX-4).

Experimental concentrations (m)		Predicted concentrations (m)				
Total sulphate	Total Th(aq)	Total Th(aq)	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
5.289×10^{-3}	9.901×10^{-8}	1.045×10^{-7}	7.266×10^{-8}	3.053×10^{-8}	1.284×10^{-9}	3.667×10^{-12}
1.058×10^{-2}	1.364×10^{-7}	1.392×10^{-7}	7.271×10^{-8}	6.129×10^{-8}	5.135×10^{-9}	2.935×10^{-11}
2.116×10^{-2}	2.155×10^{-7}	2.171×10^{-7}	7.280×10^{-8}	1.235×10^{-7}	2.055×10^{-8}	2.350×10^{-10}
3.173×10^{-2}	3.040×10^{-7}	3.065×10^{-7}	7.289×10^{-8}	1.866×10^{-7}	4.622×10^{-8}	7.924×10^{-10}
4.231×10^{-2}	4.082×10^{-7}	4.077×10^{-7}	7.299×10^{-8}	2.507×10^{-7}	8.217×10^{-8}	1.879×10^{-9}
5.289×10^{-2}	5.208×10^{-7}	5.211×10^{-7}	7.307×10^{-8}	3.159×10^{-7}	1.285×10^{-7}	3.673×10^{-9}
6.347×10^{-2}	6.369×10^{-7}	6.464×10^{-7}	7.317×10^{-8}	3.819×10^{-7}	1.850×10^{-7}	6.349×10^{-9}
7.405×10^{-2}	7.752×10^{-7}	7.844×10^{-7}	7.326×10^{-8}	4.490×10^{-7}	2.520×10^{-7}	1.009×10^{-8}
8.463×10^{-2}	9.259×10^{-7}	9.345×10^{-7}	7.336×10^{-8}	5.170×10^{-7}	3.291×10^{-7}	1.506×10^{-8}
9.520×10^{-2}	1.089×10^{-6}	1.098×10^{-6}	7.344×10^{-8}	5.862×10^{-7}	4.167×10^{-7}	2.145×10^{-8}
1.058×10^{-1}	1.261×10^{-6}	1.274×10^{-6}	7.354×10^{-8}	6.563×10^{-7}	5.147×10^{-7}	2.946×10^{-8}

[1972SAT]

This letter to the editor provides no thermodynamic information. The author has used experimental determination of the molar compressibility to calculate hydration numbers of different metal ions, including Th^{4+}. Data of this type give no information on the number of water molecules in the first coordination sphere, only an "operational" coordination number, in this case 14 for Th^{4+}. Operational coordination numbers of this type are always dependent on the method used and are therefore of limited chemical interest.

[1972USH/SKO]

The authors determined mononuclear hydrolysis constants $\log_{10} {}^*\beta_{1,1}$ ($Th(OH)^{3+}$) and $\log_{10} {}^*\beta_{2,1}$ ($Th(OH)_2^{2+}$) in water and in aqueous ethanol mixtures containing 19.8 and 40.3 mass% ethanol at I = 0.05 M and 25°C. Similar measurements were made for the trivalent lanthanide, yttrium, and scandium ions, which do not concern this review. Usherenko and Skorik [1972USH/SKO] observed a linear relationship between $\log_{10} \beta^{\circ}_{1,1}$ ($Th(OH)^{3+}$) and the reciprocal of the dielectric constant of the solvent.

The present review considers only the hydrolysis constants for Th^{4+} in aqueous solution reported in [1972USH/SKO]:

$\log_{10} {}^*\beta_{1,1}$ ($Th(OH)^{3+}$, $I = 0.05$ M) = $-(3.15 \pm 0.07)$ $\log_{10} {}^*\beta^{\circ}_{1,1} = -2.63$,

$\log_{10} \beta^{\circ}_{1,1} = 11.36$

$\log_{10} {}^*\beta_{2,1}$ ($Th(OH)_2^{2+}$, $I = 0.05$ M) = $-(6.56 \pm 0.16)$ $\log_{10} {}^*\beta^{\circ}_{2,1} = -5.70$,

$\log_{10} \beta^{\circ}_{2,1} = 22.28$.

The conditional equilibrium constants were determined by potentiometric titration at a single thorium concentration of 5 mM using 0.01 M CO_2-free NaOH. Titrations were performed under Ar atmosphere; ionic strength was kept constant at $I = 0.05$ M with NaCl and $NaClO_4$. The H^+ concentration was measured with glass and Ag/AgCl reference electrodes calibrated by titrating HCl standard solutions. The acid concentration of the initial thorium perchlorate solutions was determined by titration in the presence of sodium oxalate. The primary experimental data, the number of titrations and the pH range investigated are not given in [1972USH/SKO]. The reported equilibrium constants at zero ionic strength were calculated using Davies equation and $\log_{10} K^{\circ}_{w} = -13.99$ for the ion product of water.

The results reported by Usherenko and Skorik [1972USH/SKO] are of a reasonable order of magnitude. However, the possible formation of polynuclear thorium hydroxide complexes is not taken into account by the authors. This would have required additional studies at different total thorium concentrations. Therefore the reported results are not considered by the present review in the selection of data for thorium hydroxide complexes.

[1973ACK/RAU2]

The Th-O system was studied by investigating the vaporisation behaviour of the dioxide phase and the univariant system, Th(1) + ThO_2(cr). A combination of mass effusion and time-of-flight mass-spectrometric techniques was employed to yield an internally consistent set of thermodynamic data. The thorium used was crystal-bar material with fewer than 200 ppm total impurities, which was also used for the preparation of ThO_2(cr).

Th(l) was contained inside a ThO_2 cup inside the tungsten effusion cell. The ionisation currents of ThO^+(g) and Th^+(g) were measured over the univariant diphasic system were determined from 1780 to 2420 K, thus including ranges where the thorium is both solid and liquid. The total effusion rate of thorium-bearing species from the same sample was measured (in a different apparatus) from 2080 to 2214 K by the collection of a known fraction of the effusate on quartz targets and subsequent determination of the thorium by activation analysis. From the mass-spectrometric results, it is clear that ThO(g) is the only species which contributes significantly to the mass effusion rate. The mass-spectrometric results were then normalised to the mass-effusion results to give the equation for the partial pressure of ThO(g) over the system Th(l)-ThO_2(cr): $\log_{10} p_{\text{ThO}} / \text{bar} = -28630/T + 7.585$. The normalised pressure of Th(l) is identical to that over pure Th(cr or l) within experimental error and since the solubility of Th in

ThO_2(cr) is insignificant in this temperature range, the activities of the coexisting liquid metal and dioxide phases below 2400 K are essentially unity.

Measurements of the ion intensities of the species in the isomolecular exchange reaction YO(g) + Th(g) $\rightleftharpoons$ ThO(g) + Y(g) were carried out using a mixture Y_2O_3 and Th held in a single-crystal Ta cup inside a tungsten effusion cell from 1930 to 2280 K. With the reasonable assumption that the instrumental sensitivities cancel for such a simple isomolecular reaction, the equilibrium constant was equated to the corresponding intensity ratio $\log_{10} K = -9020/T - 0.496$ (1930–2280 K).

The congruently vaporising composition of thoria was measured from both the O and Th-rich sides by analysing the residues from samples heated in a tungsten cell for 3–6h, followed by measurement of the weight gain on combustion in air at 1673 K. At 2820 K, the congruently vaporising composition was shown to be $ThO_{(1.994\pm0.002)}$.

These results were combined by the authors with thermal functions for the species involved to evaluate the standard Gibbs energy of formation of ThO(g) from 1600 to 3000 K. The authors then re-evaluated the measurements of Ackermann *et al.* [1963ACK/RAU] on the total effusion rate of the vaporisation of ThO_2(cr), to calculate the individual partial pressures of ThO_2(g), ThO(g), and O(g) over the congruently evaporating dioxide phase and thus standard Gibbs energy of formation of the gaseous dioxide.

This is a high quality study, whose results are included in the analysis of the data for ThO(g) and ThO_2(g) in Section VII.1.

[1973ACK/RAU3]

This study is centred on the identification of the thermal decomposition products of the residue formed upon dissolution of thorium and uranium metals in hydrochloric acid. The authors first confirmed earlier studies [1962KAT/KAP] which showed that such residues correspond to an oxide hydride containing chloride and hydroxide ions. They showed, that, in the case of thorium, the ultimate decomposition product upon heating in air at 1173 K was ThO_2(cr) and that HCl was evolved in this reaction. They also studied by X-ray diffraction samples of the decomposition products of both (thorium and uranium) residues heated *in vacuo* at 1073 K for 4 hours in tungsten crucibles. In the case of thorium, they identified two sets of diffraction lines, the most intense set corresponding to ThO_2(cr) and the other set, about 10% as intense as that of ThO_2(cr), was consistent with a cubic face centred structure with $a = (5.302 \pm 0.003)$ Å which they tentatively ascribed to ThO(cr). The authors suggested that given the quantity of this phase and the purity of the original metal samples the amounts of carbon and nitrogen in this phase would be very low. Some support for the existence of a ThO(cr)-based phase was obtained from high temperature diffractometer data, in which the decomposition of the thorium residue began to show, at 973 K, the simultaneous presence of ThO_2(cr) and, as a very minor constituent, ThO(cr). This minor constituent persisted up to 1273 to 1473 K, at which point the intensity of the lines of face centred cubic thorium metal began to increase. One line attributed to ThO(cr), in the presence of lines due to Th(cr) and ThO_2(cr), was also shown on a low angle diffractometer trace of a sample heated at about 1373 K for half an hour and then cooled to room temperature. These results are consistent with the high temperature decomposition of a ThO(cr)-based phase into, essentially, the metal and the dioxide, although, in spite of the confidence expressed by the authors, the presence of light element impurities (carbon, nitrogen…) and possibly tungsten, could have played a role in stabilising the ThO(cr) phase. In any case, it seems clear that pure ThO(cr) is not a stable phase in the binary Th-O phase diagram.

In the case of the uranium residue the results were indicative of an analogous decomposition process upon heating.

[1973DER/FAU]

This is a preparative study where the authors have identified a number of different carbonate phases and determined their analytical composition and unit cells. The following Th(IV) phases have been identified: $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot 4H_2O$; $[C(NH_2)_3]_4[Th(CO_3)_4]\cdot 6H_2O$; $[C(NH_2)_3]_2[Th(CO_3)_3]\cdot 4H_2O$; $Na_6[Th(CO_3)_5]\cdot 12H_2O$; $Na_4[Th(CO_3)_4]\cdot 7H_2O$. Only the penta-carbonates were obtained in crystalline form.

[1973DER/FAU2]

The authors have used four different methods, potentiometry (measurement of the hydrogen ion concentration), cryoscopy (measurement of freezing point depression), conductometry and ion exchange, to determine the stoichiometry of the complexes formed in the Th(IV)-carbonate system. The experiments have not been made at constant ionic strength and no equilibrium constants have been proposed. However, the authors proposed the formation of three different complexes $Th(CO_3)_4^{4-}$, $Th(CO_3)_5^{6-}$, and $Th(CO_3)_6^{8-}$. In two previous studies [1962FAU/DER], [1962FAU/DER2] they specifically stated that both the cryoscopic and the potentiometric data were only consistent with the penta-carbonato complex as the limiting species. This complex was confirmed in the potentiometric study presented and identified using the inflexion point in the titration and this qualitative observation is accepted by this review. The conductometric titration data also show slope changes that Dervin and Faucherre interpret as a result of changes in the speciation. However, in order to validate this suggestion it is necessary to compare the experimental data with calculated data obtained using different speciation models, this has not been done and accordingly even the qualitative observations are not accepted by this review. The distribution coefficient of Th(IV) between an aqueous phase and an anion exchange phase (Dowex 1X8) was measured as a function of the carbonate concentration. Analysis of the slope of $\log_{10} D$ *vs.* $\log_{10}[CO_3^{2-}]$ was interpreted qualitatively and the authors suggested the formation of the complexes $Th(CO_3)_5^{6-}$, and $Th(CO_3)_6^{8-}$. This review does not accept this interpretation. The latter complex is an artefact arising from activity coefficient variations due to changes of the solution composition (*cf.* the discussion in Section XI.1.3.3).

[1973DER/FAU3]

The solubility of the previously identified [1973DER/FAU] solid thorium(IV) pentacarbonato phases $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ and $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ has been measured as a function of the bicarbonate and carbonate concentration in nitrate media of constant concentration of the corresponding cation, $[C(NH_2)_3^+] = 2.0$ M and $[Na^+] = 2.0$ M, respectively. The experimental data refer to the reaction:

$$M_6[Th(CO_3)_5]\cdot xH_2O(s) \rightleftharpoons 6M^+ + Th(CO_3)_n^{4-2n} + (5-n)\,CO_3^{2-} \qquad (A.61)$$

where the value of n can be determined from a slope analysis and the solubility constant from the measured solubility.

In the first set of data the solid phase was $[C(NH_2)_3]_6[Th(CO_3)_5](s)$ and the solubility was measured using a guanidinium nitrate ionic medium:

1) 2.0 M $C(NH_2)_3(HCO_3\text{-}NO_3)$ solutions with $[HCO_3^-] = 0.2-1.0$ M and $I = 2.0$ M
2) $(C(NH_2)_3)_2CO_3\text{-}C(NH_2)_3NO_3$ solutions with $[C(NH_2)_3^+] = 2.0$ M, $[CO_3^{2-}] = 0.25-1.0$ M and $I = 2.25-3.0$ M

The solubility of $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ in 2.0 M $C(NH_2)_3(HCO_3\text{-}NO_3)$ solution had a constant value: $[Th(CO_3)_5^{6-}] = 1.57\times 10^{-3}$ M. From these data we obtain the equilibrium constant $K_{s,5} = [C(NH_2)_3^+]^6[Th(CO_3)_5^{6-}] = 0.10\ M^7$ ($\log_{10} K_{s,5} = -1.00$) for the reaction:

$$[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s) \rightleftharpoons 6C(NH_2)_3^+ + Th(CO_3)_5^{6-} + xH_2O(l) \qquad (A.62)$$

The solubility in the $C(NH_2)_3)_2CO_3\text{-}C(NH_2)_3NO_3$ solutions remained constant at 1.7×10^{-3} M, in the range $0.25\ M < [CO_3^{2-}] < 0.35$ M, indicating the predominance of $Th(CO_3)_5^{6-}$ in solution and $K_{s,5} = [C(NH_2)_3^+]^6[Th(CO_3)_5^{6-}] = 0.109\ M^7$ ($\log_{10} K_{s,5} = -0.98$), consistent with the value in the bicarbonate solutions. At higher carbonate concentrations the solubility increases with the slope +1 apparently indicating an equilibrium between $Th(CO_3)_5^{6-}$ and $Th(CO_3)_6^{8-}$. The authors propose the reaction:

$$Th(CO_3)_5^{6-} + CO_3^{2-} \rightleftharpoons Th(CO_3)_6^{8-} \qquad (A.63)$$

As shown below for the analogous results with $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ it is clear that the activity coefficients do not remain constant at these high and varying carbonate concentrations and this review therefore does not accept the interpretation given by Dervin and Faucherre. It is not possible to extrapolate the conditional solubility constant $\log_{10} K_{s,5}$ ($I = 2$ M) to zero ionic strength, because the ion interaction coefficients between $C(NH_2)_3^+$ and NO_3^-, HCO_3^-, CO_3^{2-}, and $Th(CO_3)_5^{6-}$ are not known.

In a second set of solubility experiments the solid phase was

$Na_6[Th(CO_3)_5]\cdot12H_2O(s)$; this is about 10 times more soluble than the guanidinium phase and accordingly the variation in ionic strength is larger. The solubility was measured in following media:

1) 2.0 M $Na(HCO_3\text{-}NO_3)$ solution ($I = 2.14$ mol·kg^{-1}); $[HCO_3^-] = 0.2-1.0$ M

2) $Na_2CO_3\text{-}NaNO_3$ solutions with $[Na^+] = 2.0$ M, $[CO_3^{2-}] = 0.15-1.0$ M and $I = 2.15-3.0$ M.

Dervin and Faucherre noted that the solubility remained constant (0.021 M) in the bicarbonate solutions and at carbonate concentrations below 0.40 M where the predominant complex is $[Th(CO_3)_5^{6-}]$ and calculated the corresponding solubility constant, $K_{s,5} = [Na^+]^6[Th(CO_3)_5^{6-}] = 1.34$ M^7 ($\log_{10} K_{s,5} = 0.13$). In both sets of experiments the ratio carbonate to bicarbonate was varied and the results indicated that no ternary hydroxide-carbonate complexes were formed.

This review uses equation (A.64) for the calculation of the solubility constant $\log_{10} K^{\circ}_{s,5}$ at zero ionic strength from the conditional equilibrium constant $\log_{10} K_{s,5}$ in 2.0 M $Na(HCO_3\text{-}NO_3)$:

$$\log_{10} K^{\circ}_{s,5} = \log_{10} K_{s,5} - 42D + 6\,\{\varepsilon(Na^+, HCO_3^-)\cdot m_{HCO_3^-} + \varepsilon(Na^+, NO_3^-)\cdot m_{NO_3^-}\} + \varepsilon(Th(CO_3)_5^{6-}, Na^+)\cdot m_{Na^+} + 12\log_{10} a_w \quad \text{(A.64)}$$

The increase of the Na^+ concentration and ionic strength caused by the dissolution of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ has to be taken into account and the data have to be converted to the molal scale. With $\log_{10} K_{s,5} = 0.49$ (molal scale) and $I = 2.61$ mol·kg^{-1} ($D = 0.240$), $\varepsilon(Na^+, HCO_3^-) = (0.00 \pm 0.02)$ kg·mol^{-1}, $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(Th(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.15)$ kg·mol^{-1}, and the water activity $a_w = 0.9385$ we obtain: $\log_{10} K^{\circ}_{s,5} = -(11.0 \pm 0.5)$.

A mean value of $\log_{10} K^{\circ}_{s,5} = -(11.2 \pm 0.4)$, is obtained from the solubility data in $Na_2CO_3\text{-}NaNO_3$ solutions according to equation (A.65):

$$\log_{10} K^{\circ}_{s,5} = 6\log_{10}[Na^+] + \log_{10}[Th(CO_3)_5^{6-}] - 42D + 6\,\varepsilon(Na^+, CO_3^{2-})\cdot m_{CO_3^{2-}} + {} + \varepsilon(Th(CO_3)_5^{6-}, Na^+)\cdot m_{Na^+} + 12\log_{10} a_w \quad \text{(A.65)}$$

with $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(Th(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.15)$ kg·mol^{-1}. This mean value is close to that calculated from the data reported in [1961LUZ/KOV], $\log_{10} K^{\circ}_{s,5} = -(11.3 \pm 0.3)$. The $\log_{10} K^{\circ}_{s,5}$ values calculated from the solubility experiments with $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ in bicarbonate [1973DER/FAU3] and carbonate solutions [1961LUZ/KOV2], [1973DER/FAU3] are accepted by this review and used to select thermodynamic data for this solid phase.

The consistency of the $\log_{10} K^{\circ}_{s,5}$ values obtained from all experimental data over the whole carbonate concentration range (Table A-41) shows that the observed increase of the solubility at $[CO_3^{2-}] > 0.3$ M, is not caused by the formation of $Th(CO_3)_6^{8-}$ as assumed by Dervin and Faucherre [1973DER/FAU3] but by the variation of the activity coefficients as a consequence of the composition of the medium and the very large Debye-Hückel term (−42 *D*).

Table A-41: Evaluation of $\log_{10} K^{\circ}_{s,5}$ ($Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$) from the solubility data of [1973DER/FAU3] in Na_2CO_3-$NaNO_3$ solution.

Molar concentrations ($mol\cdot L^{-1}$)			m_i/c_i	I_m	a_w	$\log_{10} K_{s,5}$	$\log_{10} K^{\circ}_{s,5}$ [a]
[Na_2CO_3]	[$NaNO_3$]	[Th]	($L\cdot kg^{-1}$)	($mol\cdot kg^{-1}$)			
	2.00		1.0692		0.939		
0.15	1.70	0.0215	1.0602	2.76	0.942	0.48	– 11.19 ± 0.46
0.20	1.60	0.0215	1.0572	2.80	0.944	0.47	– 11.21 ± 0.44
0.25	1.50	0.0215	1.0543	2.85	0.945	0.46	– 11.23 ± 0.43
0.30	1.40	0.0215	1.0513	2.89	0.946	0.45	– 11.25 ± 0.42
0.40	1.20	0.025	1.0453	3.07	0.949	0.54	– 11.24 ± 0.39
0.50	1.00	0.029	1.0393	3.24	0.951	0.61	– 11.23 ± 0.38
0.60	0.80	0.033	1.0333	3.40	0.954	0.67	– 11.22 ± 0.36
0.70	0.60	0.036	1.0273	3.56	0.956	0.72	– 11.22 ± 0.35
0.80	0.40	0.040	1.0214	3.71	0.959	0.76	– 11.22 ± 0.35
0.90	0.20	0.043	1.0154	3.86	0.961	0.80	– 11.22 ± 0.35
1.00	0.00	0.046	1.0094	4.00	0.964	0.83	– 11.22 ± 0.35

a: The large uncertainties arise from the ionic strength corrections (error propagation accounting for the uncertainties of the SIT coefficients)

[1973FUG/BRO]

The enthalpies of solution of the following halides in 1 and 6 M HCl were measured at (298.15 ± 0.05) K:

Table A-42: Enthalpy of solution ($kJ\cdot mol^{-1}$) of β-$ThCl_4$, β-$ThBr_4$, ThI_4(cr), UBr_4(cr), UI_4(cr) and $NpBr_4$(cr) in 1 and 6 M HCl.

	1 M HCl	6 M HCl		1 M HCl	6 M HCl
$ThCl_4$(β)	– 241.8 ± 0.7	– 188.3 ± 0.4	$ThBr_4$(β)	– 283.2 ± 1.3	– 233.9 ± 0.8
ThI_4 (cr)	– 322.0 ± 0.6	– 276.0 ± 1.2	UBr_4(cr)	– 264.6 ± 0.5	– 205.7 ± 0.9
UI_4(cr)	– 289.9 ± 1.3	– 240.2 ± 1.3	$NpBr_4$(cr)	– 258.8 ± 0.5	– 199.2 ± 0.4

The concentrations of the various actinide halides in the solutions were in the 1 to 3 millimolar range.

The results reported in this study are for very pure samples prepared in duplicate and characterised by X-ray data and gravimetric/titrimetric techniques. Uncertainty limits are reported for the 95% confidence interval.

In conjunction with results from [1949WES/ROB3], [1950EYR/WES], and [1969SMI/THA], and of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (ThCl$_4$, β, 298.15 K), these data are used for the determination of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (Th^{4+}, 298.15 K). They serve also as basis for the selection of the enthalpies of formation of β-ThBr$_4$ and ThI$_4$(cr).

[1973ONO/KAN]

Ono *et al.* have measured the heat capacity of ThN(cr) and Th$_3$N$_4$(cr) *in vacuo* from 450 to 850 K, using a high temperature double-adiabatic calorimeter, with synthetic sapphire and 'reactor grade' ThO$_2$(cr) as standards. The samples were prepared from Th(cr) by hydrogenation and reaction with N$_2$(g), and were analysed for Th and N, the derived compositions being ThN$_{0.95}$ and Th$_3$N$_{3.93}$. The ThO$_2$ content of the final samples was indicated to be < 2%; no corrections were made for this.

Individual experimental data are not reported, but the results are presented as small diagrams and as fitted equations for the range 298.15 K < T < 850 K. As noted in Section X.1, their derived heat capacity equations give somewhat lower values of $C_{p,\mathrm{m}}^{\circ}$ at 298.15 K than those derived from low-temperature measurements [1972DAN/NOV], [1973DEL], so the authors' data have been refitted with constraints of $C_{p,\mathrm{m}}^{\circ}$ (298.15 K) equal to these values. The equations have been extrapolated to 2000 K in order to process the Th$_3$N$_4$ dissociation pressure data to derive a value for the enthalpy of formation of ThN(cr).

[1973SAT/KOT]

The authors have studied the distribution of Th(IV) between an aqueous phase containing hydrochloric acid, potassium thiocyanate and tricaprylmethylammonium chloride (TCA-Cl) into benzene. TCA acts as a liquid ion exchanger according to:

$$\mathrm{SCN^-(aq) + TCA\text{-}Cl(org) \rightleftharpoons TCA\text{-}SCN(org) + Cl^-(aq)} \qquad (A.66)$$

This equilibrium was studied in a first set of experiments without Th(IV). In a second set of experiments the distribution coefficient of Th(IV) between an aqueous phase and benzene was measured at different concentrations of KSCN (0.2 − 2 M). The total concentration of Th(IV) was 0.0026 M, of TCA-Cl 0.094 M and HCl between 0.05 and 0.4 M. The stoichiometry of the extracted Th(IV) complex was determined in test solutions where the KSCN concentration was 1 M and the extraction reaction was:

$$\mathrm{Th(SCN)_6^{2-}(aq) + 2TCA\text{-}SCN(org) \rightleftharpoons (TCA)_2\,Th(SCN)_6^{2-}(org) + 2SCN^-(aq)} \qquad (A.67)$$

The absorption and IR spectra in both the aqueous and the organic phase were consistent with the extraction equilibrium (A.67). There is no quantitative information on the equilibrium constant for Reaction (A.67) or for the complex formation reactions in the aqueous phase.

[1973SKE/PAT]

The Gibbs energy of formation of ThF_4 was determined from 961 to 1076 K with emf cells using a CaF_2 solid electrolyte and Ni/NiF_2 as the counter electrode. The ThF_4 used contained up to 500 ppm Ca and 100 − 120 ppm Mg and Si. Reaction between ThF_4 and CaF_2 was minimised by using a single crystal of CaF_2 as the electrolyte. Symmetrical double cells provided a continuous check on the absence of thermal gradients and data reproducibility. Initial stable emfs were obtained within a few hours, and in 0.5 − 1 h after a change in temperature.

The results are presented only in the form of graphs and equation of the emf as a linear function of the temperature. The data are analysed by the third-law in Section VIII.1.1.2.3.

[1974BIN/SCH2]

The vapour pressure of $ThCl_4$(cr) was measured from 559 to 702 K by mass-spectrometric Knudsen effusion. No details whatever are given of the $ThCl_4$ sample used. No absolute measurements were made but approximate pressures were determined by calibration with a zinc standard. However for these pressures, the plot of $\log_{10}p$ *vs.* $1/T$ has a noticeable curvature, attributed to unspecified experimental errors. The authors therefore preferred to combine their experimental pressure $\log_{10}p/\text{bar} = -7.2597$ at 636.4 K, the weighted mean temperature of their measurements, with an extrapolation of the measurements of [1939FIS/GEW2] (at the appreciably higher temperatures of 974 to 1036 K) by assuming $\Delta_{\text{sub}}C_{p,\text{m}} = (-17.41 - 13.8\times10^{-3}\ T)\ \text{J·K}^{-1}\text{·mol}^{-1}$, based on the data for the sublimation of $ZrCl_4$ from the 1971 JANAF tables. The sublimation enthalpy and entropy at 298.15 K were calculated.

Given the lack of information on the sample, the difficulties of mass-spectrometric pressure calibrations, and the admitted unknown experimental errors, these data have been given low weight in the assessment of the sublimation data. The pressures calculated by calibration with zinc are included on Figure VIII-6 for comparison with the more precise data.

[1974GAB/REE]

This is a comprehensive study of the infra-red spectra of ThO_2(g) (and some lanthanide oxides), vaporised from iridium or tungsten cells and condensed into argon matrices. Oxides substituted with ^{18}O were also studied, so that the observed frequency shifts for the isotopomers could be compared with those calculated from a normal co-ordinate analysis. The observed frequencies of ν_1 and ν_3 of 787.4 and 735.3 cm^{-1} for $Th^{16}O_2$ were consistent with a bent molecule with a O–Th–O angle of (122.5 ± 2.0)°. The frequencies are essentially the same as those found by Linevsky [1963LIN], using a lower resolution spectrometer, although he inferred an interbond angle of (106 ± 10)°.

For ThO(g), the values obtained for ω_e and $\omega_e x_e$ of (883.8 ± 1.8) and (1.9 ± 0.9) cm^{-1} are reasonably close to those found from the detailed analysis of the vapour (895.77 and 2.39 cm^{-1}) [1985EDV/LAG2] and references quoted therein.

[1974HIL/MUR]

High temperature mass spectrometric measurements were made on the equilibria $0.5\text{Th(cr)} + 0.5\text{ThO}_2\text{(cr)} \rightleftharpoons \text{ThO(g)}$ from 1782 to 1940 K and $\text{ThO(g)} + \text{Si(g)} \rightleftharpoons \text{Th(g)} + \text{SiO(g)}$ (2064 to 2212 K).

In both reactions, a molybdenum Knudsen cell was used, inside which a rough thoria cell was made by firm tamping of ThO_2 powder. Additional material (Th(cr) for the first reaction, and MoSi_2, Th and ThO_2, with or without Mo powder, for the second reaction) were then added to this crude ThO_2 crucible.

For the first reaction, the pressures of ThO(g) (ten data points) were estimated by assuming the ionisation cross-sections for Th(g) and ThO(g) are equal, and the activity of Th(cr) was unity. With these assumptions, which the authors suggest lead to an uncertainty of ± 20% in $\log_{10} p_{\text{ThO}}$, this was given by the expression:

$$\log_{10} p_{\text{ThO}} / \text{bar} = 8.392 - 30480/T \qquad (1782 - 1940\ \text{K}).$$

For the second (isomolecular) reaction, the instrumental efficiencies are likely to cancel out and the equilibrium constants will be little different from those for the corresponding ionic reaction, and thus $\log_{10} K = -2.7216 + 1001.9/T$ (fitted by this review). All these experimental values have been included in the assessment of the data for $\Delta_f H_m^\circ$ (ThO, g, 298.15 K) in Section VII.1.1.2.

The authors also describe the difficulties in interpreting the threshold voltage for ThO ionisation.

[1974KOH/STE]

The high temperature vaporisation of the thorium-carbon systems was studied by the Knudsen effusion-mass spectrometric method. (Similar studies were carried out on the Ti-C, Zr-C and Hf-C systems, which do not concern the present review). The samples used were prepared *in situ* in the mass-spectrometer by heating a mixture of thorium powder with excess graphite powder in tungsten or tantalum effusion cells. Formation of the (carbon-saturated) dicarbide was verified by X-ray diffraction. Thorium dicarbide and tetracarbide species were identified in the gas phase and second- and third-law methods were used to determine the standard enthalpies for the reactions $\text{Th(g)} + 2\text{C(cr)} \rightleftharpoons \text{ThC}_2\text{(g)}$ and $\text{Th(g)} + 4\text{C(cr)} \rightleftharpoons \text{ThC}_4\text{(g)}$. The thermal functions for the gaseous carbides used in the calculations are discussed in terms of assumed molecular structures and electronic contributions to the partition functions. In addition, a maximum value was established for the dissociation energy of ThC(g).

The results from this paper, which agree within their uncertainties with the similar studies by [1980GUP/GIN] (according to these authors) and [1964JAC/BAR], are analysed in more detail in Sections XI.1.2.1 and XI.1.2.2. It is noted in these sections that recent calculations by Kovács and Konings [2008KOV/KON] indicate that ThC_2(g) and ThC_4(g) are not linear, as assumed by [1974KOH/STE], but have L-shaped and fan-shaped structures respectively. This results in considerable differences in the calculated and experimental entropies of the relevant reactions and no data are selected for ThC_2(g) or ThC_4(g) for this review.

[1974MAG/ROM]

Complex formation in the Th(IV)-azide system was studied at 25°C using potentiometric methods, *i.e.* the determination of $-\log_{10}[H^+]$ in a 3.00 M $NaClO_4$ ionic medium. Data from three series of titrations with a total concentration of Th(IV) equal to 10.00, 20.00 and 50.00 mM were used to deduce the equilibrium constants for the species $Th(N_3)_n^{4-n}$, $n = 1-2$. The hydrogen ion concentration in all experiments was larger than 1.2 mM and hydrolysis can therefore be neglected. The experimental methods used and the analysis of the data are excellent and the equilibrium constants $\log_{10}\beta_1 = (3.09 \pm 0.11)$ and $\log_{10}\beta_2 = (6.37 \pm 0.08)$ are accepted by this review. These equilibrium constants have been obtained by a least-squares fitting to the experimental data and the estimated uncertainty has been assumed by this review to be 3σ. The protonation constant for the azide ion, necessary for the analysis of the experimental data, $\log_{10}K = 4.78$ is taken from Maggio *et al.* [1967MAG/ROM].

[1974MAS/JHA]

Thorium tetrachloride has been shown to possess two polymorphic forms. The crystal structure or the β form, stable above 678 K, has been well established to be tetragonal with space group $I4_1/amd$ and lattice parameters $a = 8.486$ and $c = 7.465$ Å. The low-temperature α form, which can only be obtained if extreme care is taken in cooling the sample, has been shown to be tetragonal with space group $I4_1/a$ with $a = (6.408 \pm 0.001)$ and $c = (12.924 \pm 0.003)$ Å. The β form is isomorphous with the other actinide tetrachlorides [1968BRO]. As this is the form normally obtained at room temperature, the values for this polymorph are considered to be the standard thermodynamic data for $ThCl_4$(cr).

[1974MAS/JHA2]

Using single crystal X-ray diffraction, these authors confirmed the existence of the β tetragonal form (space group $I4_1/amd$) of $ThBr_4$(cr), and reported the lattice parameters as $a = (8.934 \pm 0.003)$ Å and $c = (7.964 \pm 0.001)$ Å. They also showed that this phase is metastable below (699 ± 5) K and identified the low temperature α form, which they obtained by careful cooling the β phase or annealing the untransformed salt for several hours in the temperature range 623 to 673 K. This α form was shown to be tetragonal, space group $I4_1/a$, with $a = (6.737 \pm 0.001)$ Å and $c = (13.601 \pm 0.003)$ Å. The two crystalline forms of $ThBr_4$ are isomorphous with the two corresponding $ThCl_4$ forms. From their DTA observations, the authors estimated that the melting point of $ThBr_4$ to be (951 ± 5) K.

[1974NEU/ZMB]

The reaction $ThO(g) + La(g) \rightleftharpoons Th(g) + LaO(g)$ was studied from 1759 to 1961 K (18 data points) in a double-focusing mass spectrometer, by heating a mixture of Th(cr) and La_2O_3(cr) in a tungsten Knudsen cell with a tantalum liner.

For the above isomolecular reaction, the instrumental efficiencies are likely to cancel out and the equilibrium constants will be little different from those for the corresponding ionic reaction, and thus $\log_{10} K = -0.78 - 14161/T$. These experimental values have been included in the assessment of the data for $\Delta_f H^\circ_m$ (ThO, g, 298.15 K) in Section VII.1.1.2. The third law enthalpy of formation of ThO(g), calculated by the review, is $-(13.0 \pm 12.9)$ $kJ\cdot mol^{-1}$ where the uncertainty is the statistical value only. Inclusion of the experimental uncertainties, mainly the ion efficiencies, is estimated to increase this to 15.0 $kJ\cdot mol^{-1}$.

[1974POY/LEB]

The emf of the cell Th(cr)| KCl-NaCl +$ThCl_{4-x}$| KCl-NaCl +$ThCl_4$|Th-Bi(l, saturated), with molybdenum conductors, was used to determine the thorium activity in Th-saturated liquid bismuth from 953 to 1093 K. The Th-Bi alloys were prepared by melting thorium chips (99.8% pure) with bismuth (99.9% pure) in BeO crucibles directly in the cell. The emf was given by $E(T) = (589 - 0.191\,T)$ mV, with a reproducibility of 5 mV. Poyarkov *et al.* suggested that the phase in equilibrium with the saturated solution was Th_3Bi_4(cr), but the more recent work by [1982BOR/BOR2] indicate that $ThBi_2$(cr) is stable up to *ca.* 1500 K and the data of [1974POY/LEB] have been assumed to refer to the partial Gibbs energy of thorium in the {Bi(l) + $ThBi_2$(cr)} phase field: $\Delta_{sln} G_m (Th) = (-224220 + 67.78\,T)$ $J\cdot mol^{-1}$. These data can be therefore be used to calculate the Gibbs energy of formation of $ThBi_2$(cr) around 1000 K. With the low solubility of thorium, the chemical potential of bismuth will be close to the ideal value and $\Delta_f G_m$ ($ThBi_2$, cr) (from Bi(l)) in the temperature range of the study by [1974POY/LEB] is calculated to be:

$$[\Delta_f G^\circ_m]^{1100\text{K}}_{950\text{K}} (\text{ThBi}_2, \text{cr}, T) = -222900 + 66.3\,T\ (\text{J}\cdot\text{mol}^{-1}).$$

As noted in Section X.5, this value is reasonably consistent with the enthalpy of formation measurements of [1982BOR/BOR2] at 300 K.

Poyarkov *et al.* [1974POY/LEB] also made measurements of the cell

Th-Zn(l, saturated)| KCl-NaCl +$ThCl_4$ |Th-Bi(l, saturated), but the analysis of these requires a knowledge of the thermodynamics of the Th-Zn system. In the light of the more direct measurements using the cell with a pure Th electrode, these data have not been utilised by the review.

The solubility of thorium in bismuth was also determined in this study. These measurements were in good accord with other data and were included in the assessment of all the solubility data by [1981CHI/AKH], mentioned in Section X.5.

[1975DAN]

The specific heat of thorium monocarbide was measured between 2 and 300 K. A sintered sample was prepared from thorium obtained by the van Arkel process and reported to contain less than 200 ppm impurities. According to chemical analyses (no details given), the overall composition of the carbide sample corresponded to $ThC_{0.965}N_{0.015}O_{0.020.}$ The lattice parameter was reported to be a = (5.3444 ± 0.0002) Å. This sample was measured over the whole temperature range 2 to 300 K.

Another ThC sample reported as "containing a larger quantity of oxygen", without more details, was measured in the temperature range 2 to 10 K; it is not clear whether any measurements were made at higher temperatures with this sample.

Up to 7 K, the specific heat data were fitted to the classical relation $C_{p,\mathrm{m}}/T = \gamma + \alpha T^2$ and a value of γ = (2.12 ± 0.04) $\mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$ was obtained with a derived Debye temperature θ_D of (262 ± 2) K. These results are in disagreement with those reported by [1964HAR/MAT], who give γ = (2.9 ± 0.2) $\mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$ and θ_D = 280 K, which the author attributed to possible differences in the stoichiometry of the samples. (A subsequent study [1979MAU/BOU] gives γ = 3.38 $\mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$ and θ_D = 238 K for $ThC_{0.75}$(cr)).

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), thus: $C^{\circ}_{p,\mathrm{m}}$ (ThC, cr, 298.15 K) = (45.1 ± 0.5) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} (ThC, cr, 298.15 K) = (58.0 ± 0.8) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. These uncertainties, although consistent with the scatter of the data presented graphically, are smaller than those suggested by the claimed precision of the calorimeter, 2 − 3% from 100 to 300 K.

These results are discussed further in Section XI.1.1.

[1975OHA/ADE]

This paper reports standard enthalpies of formation at 298.15 K, based on solution reaction or fluorine bomb calorimetry, on a series of alkali metal uranates, molybdates, chromates, Li_3N, Li_2O, $MoC_{0.502}$, $MoC_{0.651}$, U_3Si, β-US_2, and $ThS_{1.029}$.

The only compound of immediate interest for this review is the thorium monosulphide, which was studied by solution calorimetry in 6.000 M HCl.

The sample was the same as that used by Flotow *et al.* [1971FLO/OSB] for heat capacity measurements. More analytical details on the sample were given in this solution calorimetry study. It had a S/Th ratio of (1.043 ± 0.005) and was reported to contain 3.77 mass% Th_2S_3, 1.47 mass% ThOS, 88 ppm C, and 15 ppm N. The S/Th ratio of the monosulphide phase in the sample was calculated to be (1.029 ± 0.019) and the reported calorimetric results are given for $ThS_{1.029}$(cr). We therefore assume that these results refer to a measured value which has been adjusted for the presence of the impurities, although no mention is made in the paper as to the value assumed for $\Delta_f H_m^o$ (ThOS, cr, 298.15 K), which is not known experimentally.

Thus, for Reaction (A.68)

$$\mathrm{ThS_{1.029}(cr) + 4H^+ \,(in\ 6.00\ M\ HCl) \rightarrow \{Th^{4+} + 1.029H_2S\}\,(in\ 6.00\ M\ HCl) + 0.971\,H_2(g)} \qquad \text{(A.68)}$$

the authors obtained $\Delta_r H_m^o$ ((A.68), 298.15 K) = −(394.05 ± 1.84) kJ·mol^{-1}. The thorium concentration in the resulting solution was *ca.* 1.6×10^{-2} M.

Combination of this value with $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = − (758.957 ± 1.600) kJ·mol^{-1} (see Section VI.1) −neglecting small dilution effects− and with $\Delta_f H_m$ (H_2S, 6.00 M HCl, 298.15 K) ≈ $\Delta_f H_m^o$ (H_2S, aq, 298.15 K) = − (38.6 ± 1.5) kJ·mol^{-1}, from the auxiliary values selected in this review, leads to:

$$\Delta_f H_m\ (\mathrm{ThS_{1.029}, cr, 298.15\ K}) = -(404.63 \pm 2.88)\ \mathrm{kJ \cdot mol^{-1}}.$$

[1975PAL/CIR]

These authors report the enthalpies of formation of RX_3 compounds (R = Y, Th or U; X = Ga, In, Tl, Sn or Pb) as determined by dynamic differential calorimetry (integration of DTA peaks, with a calibration from elements and compounds of known heats of fusion). These studies follow previous studies by the same group on rare earth intermetallic compounds having the same general formula. The calorimetric method used is described in one of these earlier publications [1973PAL].

In the case of thorium the compounds with In, Tl, Sn, and Pb were studied. Purities of 99.95% for the thorium metal and 99.999% for the other elements used are given without further details. Samples (1 to 2 g) were obtained by mixing and pressing the powdered metals into the calorimetric molybdenum reaction chamber. Use of a dry box under ultra pure argon atmosphere was mentioned for the handling of oxidisable substances. Only results from compounds showing a single phase ($AuCu_3$ type), as verified by micrographic and X-ray analyses, were considered. Micrography could not be carried out on $ThPb_3$ and $ThTl_3$, owing to the high reactivity of these compounds. The authors indicate that several samples were prepared to test the reproducibility of the results.

The reaction temperatures were 773 K for $ThIn_3$, 843 K for $ThTl_3$, and 793 K for $ThSn_3$ and $ThPb_3$. At these temperatures, In, Tl, Sn and Pb are liquid. After correcting for the enthalpy of fusion of these elements the authors report $\Delta_f H_m^\circ$ (ThIn$_3$, cr, 298.15 K) = −(150.6 ± 15.1) kJ·mol^{-1}, $\Delta_f H_m^\circ$ (ThTl$_3$, cr) = −(103.8 ± 10.4) kJ·mol^{-1}, $\Delta_f H_m^\circ$ (ThSn$_3$, cr) = −(162.3 ± 16.2) kJ·mol^{-1} and $\Delta_f H_m^\circ$ (ThPb$_3$, cr) = −(117.2 ± 11.7) kJ·mol^{-1} to be valid at 298.15 K. The values are in fact those at the temperatures stated, and are assumed by the authors to be the same at 298.15 K. We have made the same assumption, but, in the values quoted above, have doubled the authors' uncertainty to ± 10%.

Finally, they correlate their results, together with the various literature data for the enthalpies of formation of MX$_3$ intermetallic compounds, with the atomic radii of the involved elements.

These values of the enthalpies of formation were those selected by [1982WAG/EVA].

[1975PAT/RAM]

The equilibrium constants of chloride and fluoride complexes of Th(IV) and Np(IV) have been determined using liquid-liquid extraction with the liquid ion-exchanger dinonyl naphthalene sulphonic acid as the extractant. The experiments have been made at 25°C in 2.00 M HClO$_4$ ionic medium. The liquid ion-exchanger allows efficient extraction even at high hydrogen ion concentrations. The chloride concentration was varied from 0.1 to 1.0 M, so there are large changes in composition of the ionic medium. The extraction data were described using two equilibrium constants:

$$\mathrm{Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}}; \qquad \beta_1 = (1.3 \pm 0.1)\ \mathrm{M^{-1}}$$

$$\mathrm{Th^{4+} + 2Cl^- \rightleftharpoons ThCl_2^{2+}}; \qquad \beta_2 = (0.5 \pm 0.1)\ \mathrm{M^{-2}}.$$

These equilibrium constants describe the experimental data, but the variations in the distribution coefficients can also be a result of activity factor variations in the aqueous phase.

The fluoride system was investigated by varying the total concentration of HF between 0.5 and 100 mM. In order to describe the distribution equilibria only one equilibrium constant is required:

$$\mathrm{Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+} \qquad {}^*\beta_1 = (2.7 \pm 0.14)\times 10^4.$$

This value is in good agreement with previous investigations and is accepted by this review.

[1975RAG/RAM]

The complex formation between Th(IV) and Cl$^-$, Br$^-$ and HF has been studied using liquid-liquid extraction using dinonyl naphtalene sulphonic acid (HDNNS), a liquid-cation exchanger soluble in organic solvents but not in water. The experiments have been made at 25°C and an ionic strength/ionic medium given in Table A-43. The experimental data consist of the distribution coefficient of ^{234}Th at trace concentrations as a function of the ligand concentration in test solutions where the hydrogen ion concentration was constant at values given in Table A-43. The fluoride complexes of Th(IV) are strong and therefore it was not necessary to make large changes in the composition of the ionic medium. The total concentration of HF varied from 0.05 to 1.00 mM. The situation is very different in the studies of chloride and bromide complexation; the chloride concentration varied from 0.1 to 1.0 M and the bromide concentration from 0.1 to 1.2 M. Accordingly there are large changes in the ionic medium and it is difficult or impossible to decide if the observed variation in the distribution coefficient of Th(IV) is a result of complex formation or the variation of the activity coefficients of Th^{4+} and H^+ in the distribution equilibrium (A.69). The authors have interpreted the data as being due to the distribution equilibrium:

$$Th^{4+}(aq) + 4\,HDNNS(org) \rightleftharpoons Th(DNNS)_4(org) + 4H^+(aq) \tag{A.69}$$

where (aq) and (org) denote the aqueous and organic phases, respectively. The concentration of Th^{4+}(aq) depends on the formation of complexes with Cl^- and Br^-.

The equilibrium constants are given in Table A-43; they are obtained using a graphical (Cl^-) or a least-squares method (Br^-).

Table A-43: Equilibrium constants of Th(IV) complexes with Cl^- and Br^-.

Reaction	Experimental conditions	β
$Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$	25°C, 2.00 M H^+, I = 2.00 M	(1.3 ± 0.1) M^{-1}
$Th^{4+} + 2Cl^- \rightleftharpoons ThCl_2^{2+}$		(0.25 ± 0.1) M^{-2}
$Th^{4+} + Br^- \rightleftharpoons ThBr^{3+}$	25°C, 0.6 M H^+, I = 1.00 M	(0.81 ± 0.05) M^{-1}
$Th^{4+} + 2Br^- \rightleftharpoons ThBr_2^{2+}$	–"–	(0.20 ± 0.04) M^{-2}

The question is now if one should describe the observed variation in the distribution equilibrium (A.69) as a result of complex formation or activity coefficient variations. This review has calculated the change in activity coefficients for Th^{4+} and H^+ in two test solutions, 2.00 M $HClO_4$ and 1.50 M $HClO_4$ + 0.50 M HCl using the SIT and interaction coefficients selected by this review, $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$; $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$; $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$; $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)$ kg·mol^{-1}, with:

$$D = \frac{[Th(DNNS)_4][H^+]^4}{[Th^{4+}][HDNNS]^4} \tag{A.70}$$

We can safely assume that the activity coefficients of the species in the organic phase are constant as they are uncharged and have concentrations that are not changing significantly. Hence only the activity coefficients of the aqueous species are expected to vary with the change in composition of the aqueous phase. The activity coefficients:

$$\log_{10}\gamma\,(\mathrm{Th}^{4+}) = -\,16D + \varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-)\,m_{\mathrm{ClO}_4^-} + \varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)\,m_{\mathrm{Cl}^-}$$

$$\log_{10}\gamma\,(\mathrm{H}^{+}) = -D + \varepsilon(\mathrm{H}^{+},\mathrm{ClO}_4^-)\,m_{\mathrm{ClO}_4^-} + \varepsilon(\mathrm{H}^{+},\mathrm{Cl}^-)\,m_{\mathrm{Cl}^-}$$

in the two test solutions are then:

$\log_{10}\gamma(\mathrm{Th}^{4+}, 2.13\ \mathrm{m\ HClO_4}) = -\,3.727 + 1.491 = -2.236$

$\log_{10}\gamma(\mathrm{H}^{+}, 2.13\ \mathrm{m\ HClO_4}) = -\,0.233 + 0.298 = 0.065$

$\log_{10}\gamma(\mathrm{Th}^{4+}, 1.60\ \mathrm{m\ HClO_4}, 0.53\ \mathrm{m\ HCl}) = -\,3.727 + 1.120 + 0.133 = -2.474$

$\log_{10}\gamma(\mathrm{H}^{+}, 1.60\ \mathrm{m\ HClO_4}, 0.53\ \mathrm{m\ HCl}) = -\,0.233 + 0.224 + 0.064 = 0.055.$

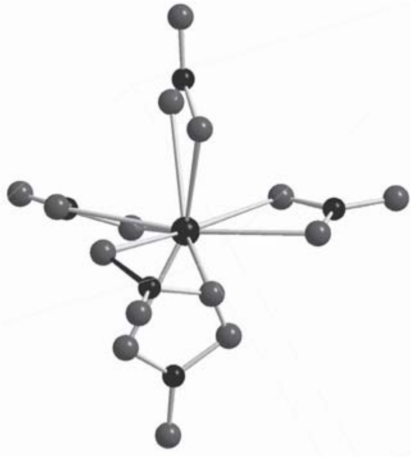
We find that, as a result of changes in activity coefficients, the value of $\log_{10} D$ should decrease by 0.198, corresponding to a decrease in D by a factor of 1.58. The experimental decrease for the chloride system from Table 1 in [1975RAG/RAM] by a factor of 1.76 is in reasonable agreement with the changes due to activity coefficient variations. However, we cannot exclude the formation of chloride (and bromide) complexes, but they are certainly smaller than the values obtained without taking ionic medium variations into account.

[1975VOL/RIM3]

This paper is discussed together with [1975VOL/RIM2].

Both these studies [1975VOL/RIM2], [1975VOL/RIM3] are single-crystal X-ray structure determinations of ternary carbonates. The structures contain isolated complexes of the complex $\mathrm{Th(CO_3)_5^{6-}}$ providing structural support of the formation of this species. The structure of the complex shown in Figure A-25 indicates that there is no space for the addition of a sixth carbonate.

Figure A-25: Structure of $\mathrm{Th(CO_3)_5^{6-}}$



The carbonate ligands form a trigonal bipyramid arrangement around Th, a geometry that is different from the more common bicapped square antiprism. The compound $Na_6[Th(CO_3)_5]\cdot 12H_2O$ has previously been described as a double-salt with the composition $Na_4[Th(CO_3)_5]\cdot Na_2CO_3\cdot 12H_2O$, [1962KAR/VOL], a proposal based on the IR spectrum of the compound. The structure is unequivocally determined by the X-ray data and the proposal by [1962KAR/VOL] demonstrates the very common fallacies of using qualitative IR data as a tool for structure assignment.

[1976BAE/MES]

Baes and Mesmer's [1976BAE/MES] comprehensive survey and critical review of the hydrolysis of cations is the most frequently cited standard book on metal ion hydrolysis and widely accepted to represent the state of the art for long time after its publication. The authors have in most cases made their own analysis of previously published data and tested a number of different equilibrium models. The choice of models is based on the standard deviation of the experimental average number of coordinated hydroxide ions $\bar{n}_{\mathrm{OH}}$. However, one should complement this method by a calculation of the speciation in the various test solutions as done in the present review. Species that occur in low concentrations should be looked upon with suspicion as gradual changes in diffusion potentials and changes in the ionic medium may be erroneously interpreted as minor complexes. The discussion of the hydrolytic behaviour of thorium(IV) is based on the following potentiometric titration studies which are also included in the data evaluation of the present review:

- [1965BAE/MEY] (including the reinterpretation of [1954KRA/HOL] data in 1 M $NaClO_4$)
- [1968HIE/SIL] (data in 3 M NaCl)
- [1968DAN/MAG] (data in 4 M $NaNO_3$ and 4 M $NaClO_4$)
- [1971MIL2] (data in 3 M $LiNO_3$, 3 M KNO_3 and 1.5 M $Mg(NO_3)_2$)
- [1971KIC/STE] (data in dilute HNO_3, HCl and $NaClO_4$, $I = 0.01 – 0.04$ M)

The selection of data is further based on solubility studies with $ThO_2(cr)$ at 95°C [1965BAE/MEY] and with $ThO_2(am, hyd)$ at 17°C [1964NAB/KUD]. The qualitative results reported in [1966HEN/JOH], [1968JOH], [1968JOH2] are also discussed.

- *Ionic strength corrections and selected values at zero ionic strength*

Baes and Mesmer used the Guggenheim equation for ionic strength corrections:

$$\log_{10} {}^{*}\beta_{n,m} = \log_{10} {}^{*}\beta^{\circ}_{n,m} + \mathrm{a}\cdot\sqrt{I}\ /\ (1 + \sqrt{I}\ ) + \mathrm{b}I,$$

with $\mathrm{a} = \Delta z^2 \mathrm{A}$ ($\mathrm{A} = 0.509\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ at 298.15 K).

The Debye-Hückel term $\mathrm{A}\cdot\sqrt{I}\ /\ (1 + \sqrt{I}\ )$, differs from the corresponding term in the SIT, $\mathrm{A}\cdot\sqrt{I}\ /\ (1 + 1.5\sqrt{I}\ )$ which leads to different values at $I = 0$ (*cf.* Table A-44).

The specific interaction parameter b is also different from the corresponding Δε value because of the different Debye-Hückel terms. Up to the review of Baes and Mesmer [1976BAE/MES], there were no data available to model the ionic strength dependence of the equilibrium constants for polynuclear species in one of the ionic media. The common method to estimate equilibrium constants at zero ionic strength was to use an experimental value at finite ionic strength and then to use only the Debye-Hückel term to estimate the value at zero ionic strength.

The selected enthalpy and entropy values for hydrolysis reactions, based on potentiometric data at 0, 25 and 95°C in 1 m $NaClO_4$, were adopted from [1965BAE/MEY].

Table A-44: Equilibrium constants $\log_{10} {}^*\beta^\circ_{n,m}$ ($Th_m(OH)_n^{4m-n}$) at I = 0 and 25°C selected by Baes and Mesmer [1976BAE/MES] and the present review.

	[1976BAE/MES]		present review
$Th(OH)^{3+}$	– 3.20 [a]		– 2.5 ± 0.5
$Th(OH)_2^{2+}$	– 6.93 [a]		– 6.2 ± 0.5
$Th(OH)_3^{+}$	≤ -11.7 [b]		No selection
$Th(OH)_4(aq)$	– 15.9 [b]		– 17.4 ± 0.7
$Th_2(OH)_2^{6+}$	– 6.14 [c]	(–5.7) [d]	– 5.9 ± 0.5
$Th_4(OH)_8^{8+}$	– 21.1 [c]	(–20.5) [d]	– 20.4 ± 0.4
$Th_6(OH)_{15}^{9+}$	–36.76 [c]	(–36.8) [d]	– 36.8 ± 1.5

a: Calculated from the equilibrium constant of [1971KIC/STE] in dilute solutions.

b: Calculated from solubility data of [1964NAB/KUD], see text.

c: Calculated from the equilibrium constant of [1965BAE/MEY] in 1 m $NaClO_4$ with b = 0.

d: Equilibrium constant of [1965BAE/MEY] in 1 m $NaClO_4$ extrapolated to I = 0 with the SIT.

- *Polynuclear hydroxide complexes*

The models proposed in the literature to describe the potentiometric data in perchlorate (1 M $NaClO_4$ [1954KRA/HOL], [1965BAE/MEY]), chloride (3 M NaCl [1968HIE/SIL]) and nitrate media (3 M $LiNO_3$, 3 M KNO_3 and 1.5 M $Mg(NO_3)_2$ [1971MIL2]) were discussed and test calculations with different sets of species were performed. The conclusions for perchlorate media are consistent with similar calculations performed in [1968HIE/SIL] and accepted in the present review. Baes and Mesmer [1976BAE/MES] selected the model including the polynuclear complexes (2,2) = $Th_2(OH)_2^{6+}$, (8,4) = $Th_4(OH)_8^{8+}$ and (15,6) = $Th_6(OH)_{15}^{9+}$. An attempt to fit the potentiometric data in 3 M NaCl [1968HIE/SIL] with the same model demonstrated that the standard deviation $\sigma(\overline{n}_{OH})$ increased to 0.033 compared to 0.014 if the species (2,2), (3,2) and (16,4) are used as proposed in [1968HIE/SIL].

On the other hand, calculations for nitrate media showed that the model selected for perchlorate media could also be applied to potentiometric data in 3 M $LiNO_3$, 3 M KNO_3 and 1.5 M $Mg(NO_3)_2$ [1971MIL2]. The resulting standard deviations $\sigma(\bar{n}_{OH})$ were found to be very small (0.0051, 0.0084 and 0.0029, respectively). Therefore Baes and Mesmer selected the model including the species (2,2), (8,4) and (15,6) as well for nitrate media. The equilibrium constants are shown in Table A-45. It is to be noted that the calculated equilibrium constants for the complexes (2,2) and (15,6), which are the same as in the models originally proposed by Milić [1971MIL2], differ only slightly from the $\log_{10} {}^*\beta_{2,2}$ and $\log_{10} {}^*\beta_{15,6}$ values calculated in [1971MIL2] in combination with the species (5,3) and (3,3) in 3 M $LiNO_3$, (3,2) in 3 M KNO_3 and (5,3) in 1.5 M $Mg(NO_3)_2$. The present review therefore also considers the proposed equilibrium constants $\log_{10} {}^*\beta_{8,4}$ as reasonable estimates.

Table A-45: Equilibrium constants $\log_{10} {}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ in nitrate media calculated by Baes and Mesmer [1976BAE/MES] from the potentiometric data of Milić [1971MIL2] at 25°C.

	3 M KNO_3	3 M $LiNO_3$	1.5 M $Mg(NO_3)_2$
$Th_2(OH)_2^{6+}$	– 5.00	– 5.12	– 5.14
	– 5.10 [a]	– 5.14 [a]	– 5.17 [a]
$Th_4(OH)_8^{8+}$	– 21.71	– 22.59	– 22.58
$Th_6(OH)_{15}^{9+}$	– 40.92	–	– 43.45
	– 40.95 [a]	–	– 43.20 [a]

a: Equilibrium constants reported in [1971MIL2].

- *Mononuclear hydroxide complexes*

Baes and Mesmer [1976BAE/MES] selected the equilibrium constants and the specific interaction parameters b for the first two mononuclear Th(IV) hydroxide complexes, $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$, $\log_{10} {}^*\beta_{1,1}^{o} = -(3.20 \pm 0.2)$ and $\log_{10} {}^*\beta_{2,1}^{o} = -(6.93 \pm 0.2)$, from potentiometric data in dilute solutions [1971KIC/STE] and 1 m $NaClO_4$ [1954KRA/HOL], [1965BAE/MEY]. Combining these values with the solubility data of Nabivanets and Kudritskaya [1964NAB/KUD] in 0.1 M $NaClO_4$, they calculated an upper limit of $\log_{10} {}^*\beta_{3,1}^{o}$ ($Th(OH)_3^+$) ≤ -11.7 and $\log_{10} {}^*\beta_{4,1}^{o}$ ($Th(OH)_4$, aq) = – (15.9 ± 0.3). The two latter values are not reliable. As shown later by potentiometry [1983BRO/ELL] and ultracentrifugation [2004ALT/NEC], polynuclear and colloidal Th(IV) hydroxide species are predominant at pH and Th concentrations of the saturated solutions in [1964NAB/KUD] (*cf.*, Appendix A review of [1964NAB/KUD]). Accordingly, the solubility constant derived from the experimental data in [1964NAB/KUD], $\log_{10} {}^*K_{s,0}^{o}$ (ThO_2, am, hyd) ≈ 9.4, is somewhat higher than the value calculated in the present review.

- *ThO$_2$(cr)*

For crystalline ThO$_2$(cr), Baes and Mesmer [1976BAE/MES] propose a value of $\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO$_2$, cr, 25°C) ≈ 6.6 ($\log_{10} K^{\circ}_{s,0}$ (ThO$_2$, cr, 25°C) ≈ −49.4) which is calculated from thermochemical data with reference to NBS, private communication. They also claim that this value is consistent with the experimental value determined by [1965BAE/MEY] at 95°C ($\log_{10} {}^{*}K_{s,0}$ (ThO$_2$, cr, 1 m NaClO$_4$, 95°C) = 4.26) which, extrapolated to $I = 0$ ($\log_{10} {}^{*}K_{s,0}$ (ThO$_2$, cr, 95°C) = (2.5 ± 0.3)) and to 25°C by estimating entropy changes, leads to $\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO$_2$, cr, 25°C) = (6.3 ± 0.5).

The equilibrium constant selected in [1976BAE/MES] differs considerably from the values based on the data selected in this review: $\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO$_2$, cr, 298.15 K) = (1.77 ± 1.11) or $\log_{10} K^{\circ}_{s,0}$ (ThO$_2$, cr, 298.15 K) = −(54.24 ± 1.11).

[1976CHE/WES]

The heat capacity Th(NO)$_3$·5H$_2$O(cr) has been measured in an adiabatic calorimeter between 5 and 350 K. The compound was analysed for thorium by gravimetry and for water by the Karl Fischer method, with results agreeing with theoretical values within narrow uncertainty limits. The values reported for 298.15 K are $C^{\circ}_{p,\mathrm{m}}$ = (480.74 ± 0.42) J·K^{-1}·mol^{-1}, S°_{m} = (543.08 ± 0.42) J·K^{-1}·mol^{-1} and $-(G^{\circ}_{\mathrm{m}}(298.15\,\mathrm{K}) - H^{\circ}(0))$ = (267.23 ± 0.25) J·K^{-1}·mol^{-1}.

No anomalies in the heat capacity curve were detected.

The entropy value obtained in this study is used in the determination of S°_{m} (Th^{4+}, 298.15 K).

[1976CHO/UNR]

This paper describes a study of the aqueous actinide fluoride complexes. Only the Th(IV) data will be discussed. The experiments have been made at 25°C in a 1.00 M HClO$_4$ ionic medium. For the Th(IV)-fluoride system two experimental methods were used at different temperatures: (1) potentiometry using a fluoride sensitive electrode (at 3, 25 and 47°C) and (2) liquid-liquid extraction with dinonyl naphthalene sulphonic acid (at 10, 25 and 55°C). The experimental methods are briefly described, with no information on primary experimental data. However, the work was done in a specialist laboratory and this review therefore accepts the equilibrium constants proposed as listed in Table A-47. The authors have used the temperature variation of the equilibrium constants to deduce the enthalpy and entropy of reaction, but these quantities are very uncertain due to the experimental errors. These quantities for the reaction between Th^{4+} and F^{-} calculated using the dissociation constant of HF are given in Table A-46.

Table A-46: Thermodynamic parameters for the reaction $Th^{4+} + F^- \rightleftharpoons ThF^{3+}$ at 25°C and 1.00 M $HClO_4$.

$-\Delta_r G^\circ_m$ (kcal·mol^{-1})	$\Delta_r H^\circ_m$ (kcal·mol^{-1})	$\Delta_r S^\circ_m$ (cal·K^{-1}·mol^{-1})	Method
10.12 ± 0.05	0.26 ± 0.32	34.8 ± 1.2	extraction
10.16 ± 0.06	0.56 ± 0.44	36.05 ± 1.5	potentiometry

The estimated uncertainty is too small according to this review.

However it is quite clear that the equilibrium constants vary little with the temperature as often found for reactions between hard acids and hard bases. The authors propose an electrostatic model to correlate the experimental data for the elements studied. This review accepts the equilibrium constants proposed in [1976CHO/UNR], but not the values proposed for the enthalpy and entropy of reaction.

Table A-47: $\log_{10} {}^*\beta_1$ for the reaction $Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$ studied using liquid-liquid extraction, and emf methods.

	$\log_{10} {}^*\beta_1$ (liquid-liquid extraction)		
Ionic medium	t (°C)		
1.00 M $HClO_4$	10	25	55
	4.65 ± 0.02	4.49 ± 0.03	4.33 ± 0.02
	$\log_{10} {}^*\beta_1$ (emf)		
Ionic medium	t (°C)		
1.00 M $HClO_4$	3	25	47
	4.73 ± 0.02	4.51 ± 0.02	4.45 ± 0.05

[1976MOR/MCC]

The enthalpy of solution of high purity $Th(NO_3)_4\cdot5H_2O(cr)$ was measured in 0.01 M $HClO_4$ at 293.15, 298.15, and 308.15 K. At infinite dilution, and after correction for hydrolysis, the value $\Delta_{sln}H^\circ_m$ ($Th(NO_3)_4\cdot5H_2O$, cr, 298.15 K) = $-$19.807 kJ·mol^{-1}, was reported. From this result, S°_m (Th^{4+}, 298.15 K) was calculated, based on S°_m ($Th(NO_3)_4\cdot5H_2O$, cr, 298.15 K) = (543.1 ± 0.8) J·K^{-1}·mol^{-1} from [1976CHE/WES], $\Delta_f H^\circ_m$ (Th^{4+}), a solubility of 3.7 mol·kg^{-1}, and activity coefficients calculated by Wagman (personal communication to the authors of the paper) based on the vapour pressure measurements of [1947ROB/LEV].

The solubility of $Th(NO_3)_4\cdot5H_2O(cr)$ at 298.15 K adopted by the authors was an average of earlier measurements by [1973APE/AZO] 3.74 mol·kg^{-1} and their own determination which yielded (3.66 ± 0.02) mol·kg^{-1}.

Based on the temperature dependence measurements, a value of $C^{\circ}_{p,\mathrm{m}}$ (Th^{4+}, 298.15 K) was also reported.

These results are the basis for the selected data on S°_{m} (Th^{4+}, 298.15 K) and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{Th(NO_3)_4{\cdot}5H_2O}$, cr, 298.15 K). The values for activity coefficient and solubility of $\mathrm{Th(NO_3)_4{\cdot}5H_2O(cr)}$ taken by the authors are adopted in the present review.

For $C^{\circ}_{p,\mathrm{m}}$ (Th^{4+}, 298.15 K), as discussed in [2003GUI/FAN], the more recent results of [1997HOV] are preferred, as they are obtained using differential measurements, instead of integral enthalpies of solution, under conditions minimising complexation and hydrolysis.

[1976PIA/ZAU]

This is an excellent study of the range of homogeneity of "$\mathrm{ThC_2}$(cr)", prepared from $\mathrm{ThO_2}$(cr) and C(cr) at high temperatures. Compressed samples of various initial mixtures of the two solids were heated in a high-temperature diffractometer operating between 1273 and 1473 K, in a vacuum or a low pressure of CO(g) and the lattice parameters of $\mathrm{ThO_2}$(cr) and the dicarbide monitored. In addition, the equilibrium pressure of CO(g) in the three-phase field $\mathrm{ThO_2}$(cr), C(cr) and "$\mathrm{ThC_2}$(cr)" was measured from 1738 to 2283 K, although the uncertainty in the temperature of the samples was estimated to be ± 30 K. The results are included in the discussion of $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{ThC_2}$, cr) in Section XI.1.1.3.

[1976POY/LEB]

The emf of the cell

$$\mathrm{Th(cr)}\,|\,\mathrm{KCl\text{-}NaCl + ThCl_{4-x}}\;\vdots\;\mathrm{KCl\text{-}NaCl + ThCl_4}\,|\,\mathrm{Pb\text{-}Th(l)} + \text{compound}$$

with molybdenum conductors, was used to determine the thorium activity in Th-saturated liquid lead from 949 to 1043 K. The Th-Pb alloys were prepared by melting Th (99.6% pure) with lead (99.9% pure) in BeO crucibles. The emf was given by $E(T) = 393.5 - 0.139\,T$ (mV), with a reproducibility of 2 mV. The actual compound present in the saturated solution was not identified, but was assumed to be $\mathrm{ThPb_4}$(cr), as indicated by Gans *et al.* [1966GAN/KNA] for this temperature range.

These data have thus been assumed to refer to the partial Gibbs energy of Th in the {Pb(l) + $\mathrm{ThPb_4}$ (cr)} phase field: $\Delta_{\mathrm{sol}}G_{\mathrm{m}} = -151870 + 56.646\,T$ ($\mathrm{J{\cdot}mol^{-1}}$). With the low solubility of thorium in Pb(l), (see below), the activity of lead in the melt will be very close to one and $\Delta_{\mathrm{f}}G_{\mathrm{m}}$ ($\mathrm{ThPb_4}$, cr) (from Pb(l)) in the temperature range of the study by [1976POY/LEB] is given by the same expression:

$$[\Delta_{\mathrm{f}}G_{\mathrm{m}}]^{1050\mathrm{K}}_{950\mathrm{K}}\,(\mathrm{ThPb_4},\ \mathrm{cr},\ T) = -151870 + 56.646\,T \quad (\mathrm{J{\cdot}mol^{-1}})$$

The solubility of thorium in lead was also determined in this study:

$$\log x_{\mathrm{Th}} = -\,4310/T + 1.667.$$

Thus x_{Th} (1000 K) = 0.227 at%. This value is quoted (presumably in error) in the paper to be the solubility at 1000°C, rather than 1000 K.

[1976SCH/VER]

The authors carried a series of compatibility experiments to obtain limiting values for the Gibbs energies of thorite ($ThSiO_4$), zircon ($ZrSiO_4$) and phenacite (Be_2SiO_4). All experiments were carried out at 1000 K and 1 kbar pressure. For $ThSiO_4$, approximately 100 mg of mixtures of the compounds of both the left-hand and right-hand sides of the two reactions below were heated (in separate experiments). The samples (together with *ca.* 10 mg of water) were contained in welded gold capsules and heated to *ca.* 1000 K and 1 kbar pressure for 2 to 12 weeks. After the runs, the samples were quenched and the products analysed by XRD. Although none of the reactions had gone to completion, in all cases the direction of reaction could be established unambiguously.

The results indicated that the two reactions:

$$\mathrm{CaTiO_3(perovskite) + ThSiO_4(thorite) \rightleftharpoons ThO_2(cr) + CaTiSiO_5(sphene)}$$

$$\mathrm{ThO_2(cr) + 0.5\,NaAlSi_3O_8(albite) \rightleftharpoons 0.5\,NaAlSiO_4(nepheline) + ThSiO_4(thorite)}$$

both have $\Delta_r G_m < 0$ at 1000 K and 1 kbar, and hence for the following reactions:

$$\mathrm{ThO_2(cr) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons ThSiO_4(thorite)} \qquad (A.71)$$

$$\mathrm{CaTiO_3(perovskite) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons CaTiSiO_5(sphene)} \qquad (A.72)$$

$$\mathrm{0.5\,NaAlSiO_4(nepheline) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons 0.5\,NaAlSi_3O_8(albite)} \qquad (A.73)$$

$\Delta_r G_m$ (A.72) < $\Delta_r G_m$ (A.71) < $\Delta_r G_m$ (A.73) at 1000 K and 1 kbar.

The authors used data from Robie and Waldbaum [1968ROB/WAL] for Reactions (A.72) and (A.73), adjusted to 1000 K and 1 kbar. This review has repeated these calculations using the most recent data from the same laboratory, Robie and Hemingway [1995ROB/HEM] to give the values in Table A-48.

Table A-48: Limiting Gibbs energies of reaction.

Reaction	$\Delta_r G_m$ (1000 K, 1 bar) ($kJ\cdot mol^{-1}$)	$\Delta_r G_m$ (1000 K, 1 kbar) ($kJ\cdot mol^{-1}$)
(A.72)	-15.90 ± 3.70	-15.96 ± 3.70
(A.73)	-9.70 ± 2.60	-9.67 ± 2.60

This study would thus suggest that the $\Delta_r G_m$ ((A.71), 1000 K, 1 bar) is $-(12.8 \pm 7.0)$ $kJ\cdot mol^{-1}$.

The authors reduce their data to 298.15 K assuming $\Delta_r C_{p,m}$ (A.71) to be zero, and further calculated $\Delta_f H_m$ ((A.71), 298.15 K) by estimating $\Delta_f S_m$ ((A.71), 298.15 K) to be the same as that for the corresponding reaction involving zirconium. Schuiling *et al.* [1976SCH/VER] do not quote the values used, but those from NEA data [2005BRO/CUR] would give $\Delta_r S_m$ (298.15 K) = −7.5 J·K^{-1}·mol^{-1}; $\Delta_r H_m$ (298.15 K) = − 22.9 kJ·mol^{-1} However, comparison with the enthalpy of Reaction (A.71) by [2005MAZ/USH] discussed in Section XI.2.2, suggests that the enthalpy and entropy of the two reactions are probably appreciably different, and this review has not attempted to estimate $\Delta_r H_m$ ((A.71), 298.15 K) from the data of [1976SCH/VER].

[1976SOU/SHA]

This is a study at 25°C of the adsorption of various actinides, including thorium, on to zirconium phosphate from HNO_3 solutions (0.1 to 6 M) and NH_4NO_3 solutions (0.1 to 6 M). The authors have not used a constant ionic medium and they have not taken the sorption of charged complexes into account when calculating the equilibrium constants. For this reason the equilibrium constant reported by them and given in Table A-49 are not considered reliable by this review.

The experimental data given in Table A-49 for nitrate and chloride indicate that the function Φ_1 (for notation see [1976SOU/SHA]) in both cases increases strongly with increasing ligand concentration. With the method used by the authors the slope of Φ_1 *vs.* [ligand] is equal to β_2 and the corresponding values for the nitrate and chloride systems calculated by this review are approximately 14 M^{-2} and 65 M^{-2}. These constants are much larger than those found by other authors using phase equilibrium methods in electrolyte media of constant ionic strength. This is another indication that the equilibrium constants in [1976SOU/SHA] are not reliable.

Table A-49: Equilibrium constants for Th(IV) nitrate and chloride complexes at 25°C.

Reaction	β_1
$Th^{4+} + NO_3^- \rightleftharpoons Th(NO_3)^{3+}$	2.5 M^{-1}
$Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$	2.8 M^{-1}

[1977CAT/SAT]

Samples of Th_4H_{15}(cr) and Th_4D_{15}(cr) of good crystallinity were prepared at pressures of H_2(g) or D_2(g) from 600 to 800 bar and temperatures from 1073 to 1173 K, and the composition, structure and superconducting properties of the material produced were examined. Values for the pressures at which Th_4H_{15}(cr) was formed are given as a function of temperature, but, as the authors state, because of hysteresis, these are undoubtedly not the true equilibrium pressures. Moreover, at the high temperatures involved, both the di- and higher hydride show substantial non-stoichiometry. These measurements are therefore of limited use for a reliable determination of the enthalpy of formation of Th_4H_{15}(cr).

[1977KAD/LEB]

The emf of the cell

$\text{Th(cr)}\,|\,\text{KCl-NaCl-3 wt\% ThCl}_{4-x}\,\vdots\,\text{KCl-NaCl-3 wt\% ThCl}_4\,|\,\text{Sn-Th(l) + compound}$ was used to determine the thorium activity in Th-saturated liquid tin from 952 to 1130 K. The emf was given by $E(T) = (535.1 - 0.1339\,T)$ mV, with a reproducibility of 2 mV. The actual compound present in the saturated solution was not identified by the authors. The thorium activity in the saturated solution is thus $\Delta_{\text{sol}}G_{\text{m}} = -206517 + 51.677\,T$ J·mol^{-1} in this temperature range.

With the low solubility of thorium in Sn(l), (see below), the chemical potential of tin in the melt will be close to the ideal value and if ThSn_3(cr) is 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

$$[\Delta_{\text{f}}G^{\circ}_{\text{m}}]^{1130\,\text{K}}_{952\,\text{K}}\,(\text{ThSn}_3,\text{ cr}, T) = -\,203377 + 48.762\,T \quad \text{J·mol}^{-1}$$

Kadochnikov *et al.* estimated the uncertainties in the thorium potential to be only ±400 J·mol^{-1}, but the uncertainty in the enthalpy values is much higher, ±6300 J·mol^{-1}, as quoted by the authors.

The solubility of thorium in liquid tin from 950 to 1130 K was also determined in this study to be:

$$\log x(\text{Th}) = -\,4330/T + 2.2360.$$

[1977MIL2]

This review concerns the two papers [1973MIL] and [1977MIL2]. The first paper [1973MIL] is an attempt to correlate the ionic strength/ionic medium dependence of the equilibrium constants for hydrolysis reactions with physico-chemical parameters; hydrolysis constants for Th^{4+}, UO_2^{2+} , Ni^{2+} and Pb^{2+} are used as examples. In [1977MIL2] the correlations were extended to enthalpy and entropy values for hydrolysis reactions of thorium derived from calorimetric measurements. Experimental data and numerical results are not given in this short report but in the following [1981MIL2].

The ionic medium dependence of the equilibrium constants for a metal ion, M, is calculated from the equation $Z_{\text{M}}(m) = Z_{\text{M}}(w)\text{e}^{-F(m)}$, where $Z_{\text{M}}(m)$ and $Z_{\text{M}}(w)$ denote the average number of coordinated hydroxide groups per metal-ion in the ionic medium (m) and pure water (w), respectively, $F(m) = \text{c(c)}E_{\text{h}}\text{(c)}E_{\text{h}}\text{(a)}z\text{(a)}/z\text{(c)}$, where z(a) and z(c) are the charges and c(a) and c(c) the concentrations of the anion and cation in the ionic medium and E_{h}, finally, is the solvation energy. There is no theoretical foundation for these equations; the main factor describing the medium dependence of equilibrium constants are the electrostatic interactions between the reactants and products and the medium ions, which is not considered at all in the model proposed here. It is very difficult to see why the hydration energy should be a major factor for the medium dependence as this depends mainly on interactions between the metal ions and the solvent in the first coordination sphere. The fact that Milić observes a linear correlation is no proof of the validity of the approach. Correlations should only be made when there is a theoretical basis for a functional relationship between two (or more) quantities and as indicated above this is not the case here. The application of this linear correlation to the extrapolation of conditional equilibrium constants of the thorium hydroxide complexes $Th_2(OH)_2^{6+}$ and $Th_2(OH)_3^{5+}$ in 0.5 − 3 M chloride media to zero ionic strength leads to $\log_{10} {}^*\beta^{\circ}_{m,n}$ values which differ by about one $\log_{10}$ unit from those obtained in this review using the SIT (*cf.* discussion of [1981MIL2]).

To conclude, this paper does not provide a useful method to estimate the ionic medium / ionic strength dependence of equilibrium constants and all equilibrium constants at zero ionic strength deduced by the approach in [1973MIL] are rejected by the present review.

[1978FLO/OSB]

The heat capacities of $ThH_{1.996}$(cr) and $ThH_{3.746}$(cr) were measured from 5.6 to 347 K. The samples were prepared from high purity Th(cr) whose main impurities were 85 ppm O and 23 ppm C. The heat capacities were represented by a sum of terms each of which could be extrapolated to higher temperatures (up to 1000 K). Values of $C_{p,\mathrm{m}}$ and the derived thermal functions are tabulated at round values from 5 to 350 K. The values of $C^{\circ}_{p,\mathrm{m}}$ and S°_{m} at 298.15 K are: $C^{\circ}_{p,\mathrm{m}}$ (ThH_2, cr, 298.15 K) = (36.71 ± 0.07) and S°_{m} (ThH_2, cr, 298.15 K) = (50.73 ± 0.10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$; $C^{\circ}_{p,\mathrm{m}}$ ($ThH_{3.75}$, cr, 298.15 K) = (51.32 ± 0.10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} ($ThH_{3.75}$, cr, 298.15 K) = (54.42 ± 0.11) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

These results were combined with thermochemical data derived from hydrogen dissociation pressure measurements to calculate the standard enthalpies and entropies of formation of ThH_2(cr) and $ThH_{3.75}$(cr) at temperatures from 298.15 to 1000 K.

[1978GIN]

This short paper mainly concerns the stability of ThC_3(g), which is present in very small amounts in the vaporisation of carbon-saturated ThC_2(cr), studied by mass-spectroscopic Knudsen effusion from 2542 to 2710 K. The study also measured the intensities from the ThC_2(g) molecule, but there is insufficient detail given for them to be included in the analysis in Section XI.1.2.

[1978KNA/MUN]

The authors studied the thermal dissociation of thorium iodide mass-spectrometrically, and suggested that substantial decomposition to lower iodides and iodine vapour occurs when both the solid and liquid are heated. Coarse crystals of ThI_4(cr), prepared from the elements, were used to minimise the oxygen and water contents of the samples used in the (unspecified) Knudsen cell. The variation of the intensities of the ThI_4, ThI_3, ThI_2, I_2 and I ions observed in the mass-spectrometer was studied from *ca.* 625 to 800 K.

Details of the method by which the intensities were converted to pressure are far from clear. It is indicated that $p_{\mathrm{ThI_4}}$ was obtained by calibration against the pressures (from an unspecified source) of pure liquid ThI_4, despite the fact that the authors themselves suggest that both solid and liquid ThI_4 decompose strongly on heating (although in fact this is probably not so, see below). The iodine pressures were established from a gravimetric determination of $p_{\mathrm{I_2}}$ over the two monovariant equilibria involving ThI_4(cr) + ThI_3(cr) and Th(cr) + ThI(cr). However, absolutely no details are given of these calibration data. The pressures of I_2(g) over ThI_4(cr) and ThI_4(l) given in the paper are much higher than those of ThI_4(g), especially at low temperatures.

The authors interpret the various plateaux obtained as corresponding to equilibria involving successively ThI_3(cr) + ThI_2(cr), ThI_2(cr) + ThI(cr), and ThI(cr) + Th(cr). The authors suggest from the small temperature range of stability of ThI_2(cr) that this phase disappears at higher temperature, and relate this to some small peaks observed by Scaife and Wylie [1964SCA/WYL] at 803 K, which they attribute to the reaction $2ThI_2(cr) \rightleftharpoons ThI_3(cr) + ThI(cr)$, but there is no further confirmation of this. In particular, there was no unambiguous characterisation of ThI(cr), and the fact that [1964SCA/WYL] not only found, but prepared, ThI_2(cr, β) well above 803 K seem to have been ignored. The authors also used their pressure data to calculate the enthalpies and entropies of all the iodides, but these data are much different from those that trends in the actinide series would suggest, and have not been accepted by the review

It must also be noted that a later mass-spectrometric and gravimetric study of this system at the same laboratory [1986FLE/KNA] indicates that the mass-spectrometry in the study by [1978KNA/MUN] may be flawed due to the use of bare metal heating elements. Flesch *et al.* [1986FLE/KNA] found that the iodine pressure from the decomposition of ThI_4 was, in fact, less than 10% of that of ThI_4(g). In view of this, and the reservations in the derivation of the results noted above, no data from this study has been accepted by the review.

[1978MAN/DEV]

The formation of thiocyanate complexes of Zn^{2+}, Mn^{2+}, Al^{3+}, In^{3+}, Th^{4+} and Hg^{2+} at different pressures have been investigated using Raman spectroscopy. The method requires large metal ion and SCN^- concentrations and the experiments have been made at a total concentration of M^{n+}-SCN^- of about 2.7 M by varying the ratio $[SCN^-]/[M^{n+}]$ between 0.5 and 8 and measuring the intensity of the CN stretch vibration in SCN^-; this changes significantly between free and coordinated ligand and the intensity can be used to determine the corresponding concentrations. Only the results for the Th(IV)-SCN^- system will be discussed. The authors report equilibrium constants for the formation of $Th(SCN)^{3+}$ and $Th(SCN)_3^+$ equal to $\log_{10}\beta_1 = (1.40 \pm 0.15)$ and $\log_{10}\beta_3 = (2.27 \pm 0.09)$ at 20°C and 1 atm. The data show conclusively that the thiocyanate ligand is coordinated at the nitrogen end. The fact that the authors were not able to identify the complex $Th(SCN)_2^{2+}$ is surprising and indicates that there might be some flaws in the quantitative evaluation of the experimental data. This review has therefore not used the reported equilibrium constants in the selection, but note that $\log_{10} \beta_1$ is in fair agreement with the value obtained by liquid-liquid extraction in the study of [1973SAT/KOT].

[1979BEL/SEM]

The authors have studied the vaporisation of thoria by mass-spectrometric measurements. There are very few experimental details in the paper, except that the ionising electron energy was 70 eV, much higher than that used by other workers. Both ThO(g) and ThO_2(g) were observed, but it proved very difficult to obtain stable and reliable ion currents for ThO^+(g). However, the ratio of the ion currents due to ThO^+ and ThO_2^+, after correction for fragmentation, was 0.60 at 2610 K and 0.73 at 2785 K. No absolute pressures are given for ThO_2(g), but the variation of ion current with temperature in the range 2480 to 2860 K corresponded to an enthalpy of sublimation of (684.9 ± 20.0) $kJ\cdot mol^{-1}$ at the congruently vaporising composition. This is negligibly different from ThO_2 in the temperature range used, so these results can be regarded as applying to the simple reaction $ThO_2(cr) \rightleftharpoons ThO_2(g)$. The value given is the average of seven runs carried out over a period of time, using two different mass spectrometers.

This enthalpy of sublimation has been converted to give $\Delta_{sub}H_m^o$ (ThO_2, cr, 298.15 K) = (746 ± 21) $kJ\cdot mol^{-1}$. However it is noted in Section VII.1.3.2 that there is an appreciable difference between the enthalpies of sublimation of thoria obtained using the second-law and third-law methods, so it is not surprising that this value differs noticeably from the consensus of third-law values given in Section VII.1.3.2.

[1979MAU/BOU]

The specific heats of $ThC_{0.75}$(cr), $ThC_{0.6}N_{0.4}$(cr) and ThP(cr) were measured from 2 to 15 K and the results used to calculate the Debye temperature and the density of states at the Fermi level of the three compounds.

[1979SIN/PRA]

Vapour pressures of solid and liquid thorium tetrachloride were measured at 880 − 1024, 1055 − 1126 K by the transpiration technique and from 923 − 1043, 1045 − 1161 K by the boiling point method. The $ThCl_4$ used was prepared from thorium hydride and chlorine gas at 500 K, and purified by vacuum distillation at 1000 K. The analysed Th/Cl ratio was reported to be 1/4. The container for both techniques was silica, which could perhaps have reacted with $ThCl_4$ to form $ThOCl_2$. However, the results from the two techniques are self-consistent and agree well with those by [1939FIS/GEW2] and [1989LAU/HIL]. The melting temperature and enthalpy of fusion of $ThCl_4$ were evaluated from the vapour pressure curves to be 1043 K, and (62.1 ± 3.7) $kJ\cdot mol^{-1}$, respectively.

[1979SIN/PRA2]

This is a short progress report describing measurements of the vapour pressure of ThI_4(cr) and ThI_4(l). The work was presented in a Conference paper [1980PRA/NAG] on the vaporisation of all the thorium halides, but no details are given; it has not been published elsewhere.

The measurements were made using both the transpiration and boiling temperature techniques in the temperature ranges 730 to 849 K for solid and 855 to 1044 K for liquid. The ThI_4 used for the study was prepared by the reaction of iodine gas with thorium hydride and purified by distillation; no analyses are given.

The vapour pressures obtained by the two techniques agreed within 6 − 7% over the whole temperature range. The constants A and B in the equation $\log_{10}(p/\text{atm}) = \text{A} / T + \text{B}$ are given in Table A-50.

Table A-50: Vapour pressure equations for ThI_4(cr) and ThI_4(l).

Phase	Transpiration		Boiling Temperature	
	A	B	A	B
ThI_4(cr)	− 10697	10.589	− 10316	10.122
ThI_4(l)	− 7917	7.309	− 7948	7.363

The melting temperature and enthalpy of fusion derived from the combined measurements were 853 K and 44.7 $kJ \cdot mol^{-1}$; no uncertainties are given.

[1980ACK/TET]

This paper deals principally with the thermodynamic properties of slightly hypostoichiometric thoria (with O/Th ratios down to 1.96). In particular, it treats very thoroughly the oxygen potentials and total pressure of thorium-bearing species over these oxides, together with the variation of the congruently vaporising composition and the lower phase boundary with temperature. The details of such studies are beyond the scope of the present review, but the paper does include additional measurements of the total vapour pressure over essentially stoichiometric thoria, measured by a transpiration technique. Although only the results of three measurements at 2400, 2500 and 2655 K are reported graphically, it is important to include these results, since they were obtained by a technique different from all the other studies. The authors do in fact state that their results agree with the total vapour pressures measured by Ackermann *et al.* [1963ACK/RAU] to within 10% (although the values read from the graph deviate a little more than that).

The transpiration experiments were carried out using a flow gas of hydrogen containing varying amounts of water vapour, to set up an appropriately low oxygen pressure in the system. The sintered granules of initially stoichiometric thoria were held in a tungsten crucible with a perforated base, held in a tungsten tube. The total vapour pressure was calculated from the weight-loss of the sample under investigation.

The pressures of thorium-bearing species increased by a factor of several hundred across the range of composition at temperatures from 2400 to 2655 K, due to a sharp increase of the ThO(g) contribution, consistent with the higher pressures in the presence of the strongly reducing tantalum, measured by Hoch and Johnston [1954HOC/JOH].

[1980BLA/LAG]

The heat capacities of Th_3As_4(cr) and U_3As_4(cr) were measured from 5 to 300 K. Th_3As_4(cr) was prepared by heating in a silica tube, *in vacuo* at 873 K, a mixture of the elements in a As/Th ratio of 2, to form $ThAs_2$(cr), which was decomposed to form Th_3As_4(cr) by further very slow heating up to 1273 K. X-ray investigation showed that the material was single-phase with a lattice parameter of (8.945 ± 0.005) Å, but no other analytical details were given.

Th_3As_4(cr) is non-magnetic with a smooth specific heat curve, while the uranium compound has a sharp λ-peak at 195.8 K, due to a ferromagnetic transition. The thermodynamic functions are derived and tabulated. Interpolation of the given values gives $C^{\circ}_{p,\mathrm{m}}$ (Th_3As_4, cr, 298.15 K) = 183.31 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} (Th_3As_4, cr, 298.15 K) = 274.56 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The various contributions to the specific heat of U_3As_4(cr) are discussed.

[1980BLA/TRO]

The heat capacities of UAs(cr) and ThAs(cr) were measured from 5 to 300 K, using the same equipment as in the related paper [1980BLA/LAG] by the same group. ThAs(cr) was prepared by thermal decomposition of Th_3As_4(cr) at 1673 K under a dynamic vacuum. The compound was reported as single phase with a lattice parameter of (5.976 ± 0.001) Å, but no analytical details were given. ThAs(cr) is non-magnetic with a smooth specific heat curve, while the uranium compound displays two sharp anomalies. The first, around 64 K, is ascribed to the transition from type IA to type I antiferromagnetic structure. The second anomaly, at 122.8 K, corresponds to the Néel temperature. The thermodynamic functions of the two compounds are tabulated. The values at 298.15 K are:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThAs, cr, 298.15\ K}) = 50.52\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}\ \text{and}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThAs, cr, 298.15\ K}) = 79.79\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The experimental result on the specific heat of UAs(cr) as a function of temperature is discussed in detail.

[1980CAE/CAS]

The authors measured the partial pressures of gaseous species over the oxides La_2O_3(cr), Y_2O_3(cr), and ThO_2(cr) contained in tantalum effusion cells, in order to investigate the gettering ability of tantalum at high temperatures. For the study of ThO_2(cr), the temperature range was 2057 to 2421 K. There are no experimental details whatever in the paper, only a one sentence reference to a previous publication (by different authors, Trevisan and Depaus [1973TRE/DEP]), which indicates that the pressures were determined by mass-spectrometry, with conversion from ion intensities *via* a silver calibration. The major species in the vapour was ThO(g), the total pressure being appreciably higher than that over stoichiometric ThO_2(cr) measured in tungsten, in agreement with the work of Hoch and Johnston [1954HOC/JOH]. As expected, TaO(g) was also an present in appreciable amounts. The following equations are given for the pressures of ThO(g) and ThO_2(g) over the hypostoichiometric ThO_{2-x}(cr) formed in the tantalum cell:

$$\log_{10} p_{\mathrm{ThO(g)}} / \mathrm{bar} = -36490 / T + 9.839 \qquad 2573-2973\ \mathrm{K}$$

$$\log_{10} p_{\mathrm{ThO_2(g)}} / \mathrm{bar} = -40310 / T + 10.427 \qquad 2573-2773\ \mathrm{K}$$

Since the activity of thorium is undefined, the pressures of ThO(g) cannot be utilised to calculate the stability of this species; for ThO_2(g), third law calculations again cannot be used, since the activity of ThO_2 in the ThO_{2-x}(cr) formed is not known. However, this activity is unlikely to change appreciably with temperature, so a second law calculation can be employed, and is included in the analysis in Section VII.1.3.2.

[1980GUP/GIN]

Six gaseous carbides of thorium, ThC_n ($n = 1-6$), were identified in a Knudsen effusion mass spectrometric investigation of the vapour phase above a Th-U-Rh-graphite system at high temperatures. The ion intensities of the thorium-containing species effusing from a mixture of ThC_2, UC_2, Rh and an excess of graphite in a graphite-lined tantalum effusion cell were measured as functions of temperature at 2300−2700 K. The corresponding partial pressures were then calculated, using the $2Au(g) \rightleftharpoons Au_2(g)$ equilibrium as a standard. No individual pressures are reported, only the atomisation energies at 298.15 K and the standard enthalpies at 298.15 K for the all the reactions Th(g) + nC(graphite) $\rightleftharpoons$ ThC_n(g) (by the second and third laws), using thermal functions for the ThC_n(g) species calculated from quoted estimated parameters. The thermal functions for ThC_2(g) given by [1980GUP/GIN] are appreciably greater than those suggested by [1974KOH/STE], due to a different assumed electronic contribution, based on that for the Th^{2+} gaseous ion. It is now known that such a comparison appreciably overestimates the electronic contribution to the thermal functions of molecular ions. As noted in Section XI.1.2, recent calculations by Kovács and Konings [2008KOV/KON] indicate that ThC_2(g) and ThC_4(g) are not linear, as assumed by [1980GUP/GIN] but have L-shaped and fan-shaped structures respectively.

In the absence of detailed experimental results, no further analysis of this study is possible. However, there is an implication in the paper that their results for the Th(g) + 2C(cr) $\rightleftharpoons$ ThC_2(g) equilibrium are very similar to those of Kohl and Stearns [1974KOH/STE], although the derived third-law enthalpies of formation of ThC_2(g) are appreciably different owing to the use of different thermal functions.

[1980NAG/BHU2]

The vapour pressure of solid ThF_4(cr) was measured by the transpiration technique and that of ThF_4(l) by both transpiration and the boiling point method, with self-consistent results.

The sample of ThF_4 used in these studies was prepared from active ThO_2 and anhydrous HF at 750 − 800 K; the only analytical details are that it was shown to be more than 99.5% pure by analysis. The containers were nickel in all the studies. For the transpiration studies, it was found to be difficult to saturate the vapour using a horizontally disposed apparatus, so a vertical assembly was used. The vapour pressure of the solid was measured by the transpiration technique from 1293 to 1375 K and that of the liquid by transpiration from 1394 to 1510 K and by the boiling point method from 1395 to 1554 K, with good self-consistency. The measured pressures are *ca.* 30 − 40% higher than those obtained by [1958DAR/KEN] and [1989LAU/BRI], which agree to within a few percent.

[1980NAK/TAK]

The heat capacities of metallic uranium and thorium were determined from at 84 to 991 K by laser-flash calorimetry.

The sample of thorium used was a disk. 11 mm in diameter, weighing 2.4 g. The main impurities were 155 ppm C and 190 ppm O. Eleven series of experiments, with a total of 206 data points, were carried out.

The heat-capacity values for thorium are several percent lower than those of Griffel and Skochdopole [1953GRI/SKO] below 298.15 K and of Wallace [1960WAL] above this temperature. However, the enthalpy data at high temperature (including those published after 1980) are in good agreement with the results of [1980NAK/TAK]. A revised table of thermodynamic functions of thorium from 80 to 1000 K is given. The standard values are $C^{\circ}_{p,\mathrm{m}}$ (Th, cr, 298.15 K) = 26.24 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and S°_{m} (Th, cr, 298.15 K) = 52.64 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. These results, using very pure metal, and extending both below and above 298.15 K, are the basis for the values for the thermal functions of α-Th up to 1000 K selected by this review.

The results of [1980NAK/TAK] indicate that the excess heat capacity of thorium is not appreciable below 1000 K, in contrast with a large excess heat capacity for uranium above 300 K.

The results on uranium agree well with those in the literature.

[1980PIC/KLE]

The partial enthalpies $\Delta_{\text{sln}}H_{\text{m}}$ of solution of hydrogen in solid thorium hydrides with H/Th ratios from 0 to 2.003 were measured calorimetrically at 700 K.

The crystal bar thorium used was from the same source as that used by Flotow and Osborne [1978FLO/OSB] and contained 500 ppm total metallic impurities, 14 ppm nitrogen and 50 ppm oxygen. The authors found a sharp change in $\Delta_{\text{sln}}H_{\text{m}}$ at H/Th ≈ 0.03, associated with the formation of the dihydride. In the diphasic region $\Delta_{\text{sln}}H_{\text{m}}$ was relatively constant at *ca.* $-(75 \pm 2)$ kJ·mol^{-1} to H/Th ≈ 1.0, and then decreased slowly to *ca.* -94 kJ·mol^{-1} at the lower phase boundary of $ThH_{1.987}$(cr). In the $ThH_{2\pm x}$ single phase region, the enthalpy of solution increased rapidly to *ca.* -12 kJ·mol^{-1} at $ThH_{2.003}$(cr).

By the integration of all these data the enthalpy of formation of ThH_2(cr) at 700 K was calculated to be $-(145.6 \pm 0.8)$ kJ·mol^{-1}. The equilibrium pressures of hydrogen also were determined for compositions from $1.988 < \text{H/Th} < 2.003$ within the $ThH_{2\pm x}$ single phase field. Combination of the partial Gibbs energies and enthalpies of hydrogen provides information on the entropy of solution. The partial enthalpy and entropy both change dramatically with composition from H/Th = 1.990 to 2.003.

[1980PRA/NAG]

This is a conference paper which collects information on vaporisation studies, all of which have been published in detail elsewhere, so this review is correspondingly brief. The vaporisation behaviour of thorium (and uranium) halides was investigated in the solid and liquid regions by the boiling-temperature and transpiration techniques. Both techniques were used for studies on $ThCl_4$, at 880 − 1161 K. The data derived from the two techniques agree excellently. Boiling-temperature studies were completed for ThF_4(cr), ($ThBr_4$(cr) and $ThBr_4$(l)) and (ThI_4(cr) and ThI_4(l)) at 1395 − 1554 K, 842 − 1089 K and 790 − 1044 K, respectively. All the vapour pressure data are expressed by the equation $\log_{10} p/\text{bar} = \text{A}/T - \text{B}$, with constants given in Table A-51. For convenience this includes also the reference to the fuller papers.

Table A-51: Vapour pressure of thorium halides, $\log_{10} p/\text{bar} = \text{A}/T + \text{B}$.

Species	Temperature range (K)	A	B	Primary reference
ThF_4(l)	1395 – 1554	– 14154	7.376	[1980NAG/BHU2]
$ThCl_4$(cr)	880 – 1043	– 11775	10.106	[1979SIN/PRA]
$ThCl_4$(l)	1045 – 1161	– 8023	6.656	[1979SIN/PRA]
$ThBr_4$(cr)	842 – 971	– 11411	10.656	[1980SIN/PRA]
$ThBr_4$(l)	971 – 1089	– 7813	6.946	[1980SIN/PRA]
ThI_4(cr)	790 – 853	– 10316	10.126	[1979SIN/PRA2]
ThI_4(l)	853 – 1044	– 7915	7.336	[1979SIN/PRA2]

[1980ZHI/KOL]

Only the original Russian paper with an English abstract was available to the reviewers and some details in the study may therefore have escaped our attention. The authors have studied the solubility of thorianite $ThO_2(s)$ in 0.1 M $NaClO_4$ as a function of pH at 17−25°C and at 50°C. Their experimental solubility data fall on a smooth curve with a constant solubility of $\log_{10} [Th] = -6.7$ at pH > 4; this experimental value is in the range found in many other studies, *cf.* review of [1954GAY/LEI].

The solubility measured by [1980ZHI/KOL] at pH < 2 with $ThO_2(s)$ is much lower than literature data for $Th(OH)_4(am)$; with increasing pH the two curves approach each other and at pH > 5 they are practically the same (Figure 1 in [1980ZHI/KOL]). There are only two experimental points where the equilibrium constants for the complexes $Th(OH)_n^{4-n}$, $n = 1-3$, can be obtained. The authors propose the solubility constants for the following reactions:

$$ThO_2(s) + H^+ + H_2O(l) \rightleftharpoons Th(OH)_3^+ \qquad \log_{10} {}^*K_{s,3} = -(3.30 \pm 0.07)$$

$$ThO_2(s) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq) \qquad \log_{10} K_{s,4} = -(6.66 \pm 0.06).$$

It is assumed that there are misprints on p.286 of [1980ZHI/KOL] and the $\log_{10} K_s$ values are negative, as above, and not positive as given there. Combining the equilibrium constants $\log_{10} {}^*K_{s,3} = -(3.30 \pm 0.07)$ and $\log_{10} K_{s,4} = -(6.66 \pm 0.06)$ yields the stepwise equilibrium constant $\log_{10} {}^*K_4$ for the reaction:

$$Th(OH)_3^+ + H_2O(l) \rightleftharpoons Th(OH)_4(aq) + H^+: \qquad \log_{10} {}^*K_4 = -(3.36 \pm 0.09).$$

In view of the limited experimental data in the region where these complexes are formed this review does not accept these values. The authors also discuss the standard Gibbs energy and enthalpy of formation of $ThO_2(s)$ and conclude that new experimental determinations of the standard enthalpy of formation of $ThO_2(s)$ and the hydrolysis constants of Th(IV) are necessary.

[1981BUR/KIJ2]

Enthalpies of solution of the following are reported: $GaCl_3$ and GaI_3 in water (or dilute HCl), methanol, and dimethylsulphoxide; $InCl_3$ and InI_3 in water and in several non-aqueous solvents; $ThCl_4$, ThI_4 and UCl_4 in 1 M HCl, methanol, ethanol, and dimethylsulphoxide. The main purpose of this study is the comparison of the enthalpy of solution of various halides in aqueous and non-aqueous solvents, but it also provides useful data on the enthalpy of solution of $ThCl_4(cr)$ and $ThI_4(cr)$ in 1 M HCl solution.

Commercial anhydrous thorium tetrachloride was used as received, "after purity checks". It is assumed to have been the most common β-form. Thorium tetraiodide was prepared by reaction between the metal and an excess of iodine which was removed by sublimation. The product was purified by sublimation. No analytical results were given.

The enthalpy of solution of $ThCl_4$ and ThI_4 in 1 M HCl were given as – (242.4 ± 1.9) and – (330.1 ± 2.1) $kJ\cdot mol^{-1}$, respectively, without any detail.

[1981FIS/FIN]

The enthalpy of ThO_2, sealed in tungsten, was measured from 2415 to 3400 K, using a modified high-temperature drop calorimeter. Enthalpies of a sample of molybdenum (NBS reference material) agreed within 1% of the NBS data. No details are given of the ThO_2 sample used.

These data agreed well with other experimental data where they overlapped. The enthalpy results showed there was a phase transition around 3000 K, which was attributed to an order-disorder transition, similar to those found in UO_2 and CaF_2 and other materials with the fluorite structure. The enthalpy data were combined with literature values and fitted to an expression representing the sum of an Einstein lattice contribution and a term proportional to T^2, representing the anharmonic and expansion contributions. This fitting is described in more detail by Finke [1982FIN] (see the review in this Appendix) and agrees very well with the selected values for the thermal functions of $ThO_2(cr)$ selected in this review, at least up to 2900 K.

[1981MIL2]

In three papers of Milić [1981MIL2] and Šuranji and Milić [1981SUR/MIL], [1982SUR/MIL], the hydrolytic behaviour of thorium(IV) is investigated in various chloride media at 25°C by potentiometry and in [1981MIL2] also by calorimetry.

The experimental procedures of the potentiometric studies (coulometry, pH measurements, *etc.*) and evaluation methods are well described. All titrations are performed at a single thorium concentration of 10 mM in the pH range 2.2 − 3.0 [1981MIL2] or 2.2 − 3.2 [1981SUR/MIL], [1982SUR/MIL] in following media: 0.5 − 3 M NaCl and 3 M LiCl, 3 M KCl [1981MIL2], 0.5 − 3 M LiCl, 0.5 − 3 M LiCl, [1981SUR/MIL], 0.25 − 1.5 M MCl_2 (denoted as 0.5 − 3 M (M)Cl) with M = Mg, Ca, Sr and Ba [1982SUR/MIL].

The potentiometric data were interpreted with the formation of only two dinuclear species, (2,2) = $Th_2(OH)_2^{6+}$ and (3,2) = $Th_2(OH)_3^{5+}$. Other models were not tested; however, the speciation model used is consistent with that of Hietanen and Sillén [1968HIE/SIL] in 3 M NaCl, which has been confirmed by test calculations in the review of Baes and Mesmer [1976BAE/MES] and selected in the present review. The complex (14,6) = $Th_6(OH)_{14}^{10+}$ which is also included in the selected model for chloride media is not relevant under the experimental conditions in [1981MIL2], [1981SUR/MIL], [1982SUR/MIL] (pH < 3.2), *cf.* speciation calculations in Appendix A review of [1968HIE/SIL]. The reported conditional equilibrium constants, with the statistical uncertainties given as 3σ are summarised in Table A-52.

Table A-52: Equilibrium constants $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ at 25°C reported in [1981MIL2], [1981SUR/MIL], [1982SUR/MIL].

Reference	Medium	$\log_{10}{}^{*}\beta_{2,2}(\mathrm{Th_2(OH)_2^{6+}})$	$\log_{10}{}^{*}\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}})$
[1981MIL2]	0.5 M NaCl	– 4.90 ± 0.16	– 7.72 ± 0.05
	1.0 M NaCl	– 4.88 ± 0.03	– 7.93 ± 0.13
	1.5 M NaCl	– 4.95 ± 0.15	– 8.01 ± 0.10
	2.0 M NaCl	– 5.02 ± 0.16	– 8.11 ± 0.12
	2.5 M NaCl	– 5.06 ± 0.12	– 8.12 ± 0.15
	3.0 M NaCl	– 5.08 ± 0.20	– 8.23 ± 0.18
[1981SUR/MIL]	0.5 M LiCl	–	– 7.54 ± 0.01
	1.0 M LiCl	– 5.07 ± 0.13	– 7.85 ± 0.05
	1.5 M LiCl	– 5.01 ± 0.14	– 8.01 ± 0.07
	2.0 M LiCl	– 4.99 ± 0.15	– 8.17 ± 0.10
	3.0 M LiCl	– 4.89 ± 0.07	– 8.49 ± 0.13
[1981MIL2]	3.0 M LiCl	– 5.23 ± 0.15	– 8.28 ± 0.12
[1981SUR/MIL]	0.5 M KCl	–5.84 ± 5.40 [a]	– 7.59 ± 0.03
	1.0 M KCl	– 5.14 ± 0.07	– 7.80 ± 0.11
	1.5 M KCl	– 4.92 ± 0.07	– 8.00 ± 0.04
	2.0 M KCl	– 4.97 ± 0.08	– 8.09 ± 0.05
	2.5 M KCl	– 4.89 ± 0.05	– 8.29 ± 0.05
	3.0 M KCl	– 4.92 ± 0.04	– 8.38 ± 0.06
[1981MIL2]	3.0 M KCl	– 5.04 ± 0.11	– 8.16 ± 0.17
[1982SUR/MIL]	0.25 M $\mathrm{MgCl_2}$	–	– 7.62 ± 0.01
	0.50 M $\mathrm{MgCl_2}$	– 5.12 ± 0.13	– 7.91 ± 0.05
	0.75 M $\mathrm{MgCl_2}$	– 5.01 ± 0.07	– 8.09 ± 0.04
	1.00 M $\mathrm{MgCl_2}$	– 4.93 ± 0.06	– 8.29 ± 0.07
	1.25 M $\mathrm{MgCl_2}$	– 4.90 ± 0.05	– 8.47 ± 0.09
	1.50 M $\mathrm{MgCl_2}$	– 4.90 ± 0.05	– 8.56 ± 0.09
[1982SUR/MIL]	0.25 M $\mathrm{CaCl_2}$	–	– 7.59 ± 0.01
	0.50 M $\mathrm{CaCl_2}$	– 4.96 ± 0.06	– 7.97 ± 0.05
	0.75 M $\mathrm{CaCl_2}$	– 4.95 ± 0.06	– 8.13 ± 0.05
	1.00 M $\mathrm{CaCl_2}$	– 4.97 ± 0.06	– 8.23 ± 0.05
	1.25 M $\mathrm{CaCl_2}$	– 4.92 ± 0.05	– 8.37 ± 0.07
	1.50 M $\mathrm{CaCl_2}$	– 4.92 ± 0.05	– 8.53 ± 0.11
[1982SUR/MIL]	0.25 M $\mathrm{SrCl_2}$	–5.53 max: –5.24 [a]	– 7.66 ± 0.03
	0.50 M $\mathrm{SrCl_2}$	– 5.29 ± 0.19	– 7.95 ± 0.04
	0.75 M $\mathrm{SrCl_2}$	– 5.06 ± 0.10	– 8.09 ± 0.05
	1.00 M $\mathrm{SrCl_2}$	– 4.95 ± 0.07	– 8.25 ± 0.08
	1.25 M $\mathrm{SrCl_2}$	– 4.93 ± 0.05	– 8.41 ± 0.06
	1.50 M $\mathrm{SrCl_2}$	– 4.97 ± 0.05	– 8.52 ± 0.07

(Continued on next page)

Table A-52: (Continued)

Reference	Medium	$\log_{10} {}^*\beta_{2,2}(\mathrm{Th_2(OH)_2^{6+}})$	$\log_{10} {}^*\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}})$
[1982SUR/MIL]	0.25 M $BaCl_2$	–5.56 max: –5.21 [a]	– 7.62 ± 0.04
	0.50 M $BaCl_2$	– 5.12 ± 0.15	– 7.92 ± 0.05
	0.75 M $BaCl_2$	– 5.02 ± 0.10	– 8.10 ± 0.07
	1.00 M $BaCl_2$	– 4.91 ± 0.04	– 8.29 ± 0.05
	1.25 M $BaCl_2$	– 4.90 ± 0.04	– 8.39 ± 0.07
	1.50 M $BaCl_2$	– 4.96 ± 0.04	– 8.50 ± 0.07

a Equilibrium constants are uncertain and not used in the present review.

- *Ionic strength corrections and equilibrium constants at zero ionic strength*

Šuranji and Milić [1982SUR/MIL] described the ionic strength dependence of the conditional equilibrium constants and the reaction enthalpies in all chloride media by an empirical linear correlation between $\log_{10} {}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ and a "medium factor" (defined in [1981MIL2]) that depends on the ionic medium concentration and the hydration energy of its ions. Correlations that have no theoretical foundation such as this can at best be used for interpolations, but never for extrapolations as in [1981MIL2]; the ionic strength dependence should be described by models based on the existing electrolyte theories. The model used by Milić does not even contain a Debye-Hückel terms and it is not surprising that the extrapolation to infinite dilution in Figure 6 of [1982SUR/MIL] leads to values ($\log_{10} {}^*\beta^\circ_{2,2}(\mathrm{Th_2(OH)_2^{6+}}) = -5.1$, $\log_{10} {}^*\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}}) = -7.5$) which differ by about one $\log_{10}$ unit from those evaluated in this review using the SIT. In Figure A-26 and Figure A-27 the terms ($\log_{10} {}^*\beta_{n,2} - n\log_{10}a_\mathrm{w} - z^2D$) are plotted against ionic strength I. The evaluated equilibrium constants $\log_{10} {}^*\beta^\circ_{n,2}$ and $\Delta\varepsilon(n,2)_\mathrm{Cl}$ derived from the slopes, $-\Delta\varepsilon(n,2)_\mathrm{Cl}$ for MCl media ($I = m_\mathrm{Cl}$) and $-\Delta\varepsilon(n,2)_\mathrm{Cl}/1.5$ for MCl_2 media ($I = 1.5\ m_\mathrm{Cl}$), are summarised in Table A-53.

Table A-53: Equilibrium constants $\log_{10} {}^*\beta^\circ_{n,2}$ and $\Delta\varepsilon(n,2)_\mathrm{Cl}$ ($\mathrm{kg \cdot mol^{-1}}$) evaluated with the SIT from the data of [1981MIL2], [1981SUR/MIL] and [1982SUR/MIL] at 25°C.

	$\mathrm{Th_2(OH)_2^{6+}}$		$\mathrm{Th_2(OH)_3^{5+}}$	
Data from (Ionic media)	$\log_{10} {}^*\beta^\circ_{2,2}$	$\Delta\varepsilon(2,2)_\mathrm{Cl}$	$\log_{10} {}^*\beta^\circ_{3,2}$	$\Delta\varepsilon(3,2)_\mathrm{Cl}$
[1981MIL2],[1981SUR/MIL] (NaCl, LiCl, KCl)	– 6.06 ± 0.17	0.10 ± 0.08	– 6.86 ± 0.12	0.09 ± 0.07
[1982SUR/MIL] ($MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$)	– 6.41 ± 0.22	0.00 ± 0.06	– 6.79 ± 0.08	0.18 ± 0.03
This review:	– 5.9 ± 0.5 [a]	0.14 ± 0.15 [a]	– 6.8 ± 0.2 [b]	0.15 ± 0.06 [b]

a: Evaluated in Section VII.3.4.1.1 using simultaneously the selected data in perchlorate, nitrate and chloride media.

b: Mean value considering also the value of [1968HIE/SIL] in 3 M NaCl.

The data of Milić [1981MIL2] are in reasonable agreement with those of Hietanen and Sillén [1968HIE/SIL] in 3 M NaCl, the $\log_{10}{}^{*}\beta_{2,2}$ value of [1968HIE/SIL] is about 0.3 $\log_{10}$-units higher, while $\log_{10}{}^{*}\beta_{3,2}$ is about 0.4 $\log_{10}$-units lower. The equilibrium constants $\log_{10}{}^{*}\beta_{2,2}$ in NaCl, LiCl and KCl media are included in the selection of data in Section VII.3.4.1.1. The $\log_{10}{}^{*}\beta_{2,2}$ values at $[\mathrm{MCl_2}] < 1.0$ M and hence the extrapolation to $I = 0$ are uncertain. The equilibrium constant $\log_{10}{}^{*}\beta_{2,2}^{\circ}$ is consistent with that derived in the present review from the data of [1971MIL2] in 0.5 − 3 M $NaNO_3$ media.

Figure A-26: Extrapolation of $\log_{10}{}^{*}\beta_{2,2}(\mathrm{Th_2(OH)_2^{6+}})$ and $\log_{10}{}^{*}\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}})$ in NaCl, LiCl and KCl media at 25°C [1981MIL2], [1981SUR/MIL] to zero ionic strength with the SIT. The data from [1968HIE/SIL] in 3 M NaCl are shown for comparison.

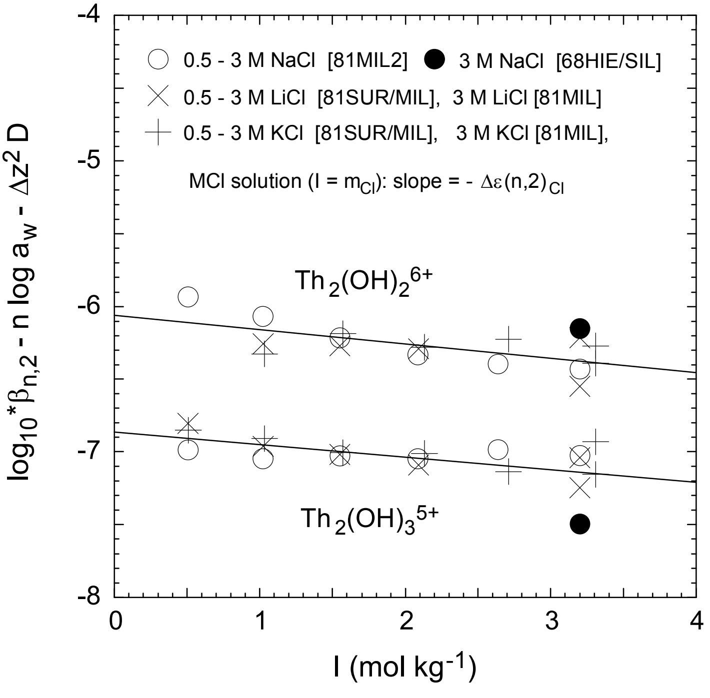
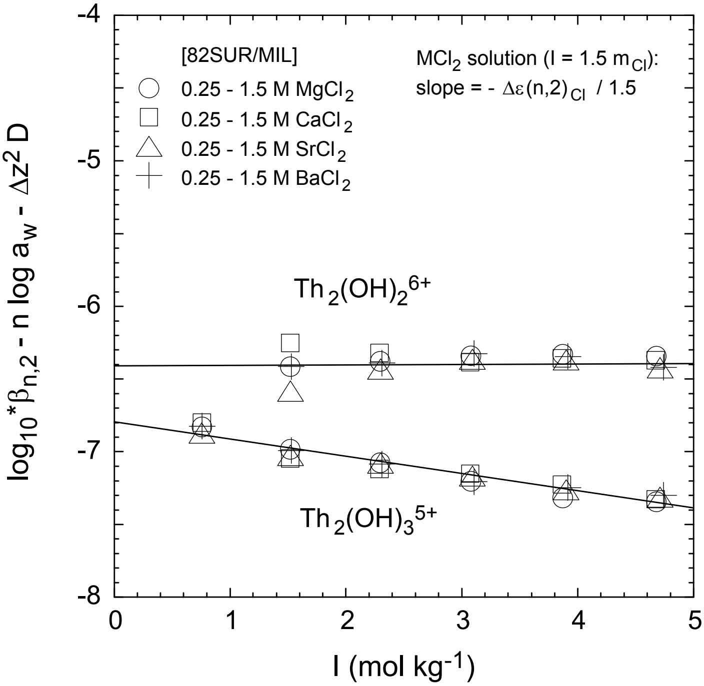


Figure A-27: Extrapolation of $\log_{10} {}^{*}\beta_{2,2}(\mathrm{Th_2(OH)_2^{6+}})$ and $\log_{10} {}^{*}\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}})$ in MCl_2 (M = Mg, Ca, Sr, Ba) media at 25°C [1982SUR/MIL] to zero ionic strength with the SIT.



The equilibrium constant $\log_{10} {}^{*}\beta^{\circ}_{3,2}$ and $\Delta\varepsilon(3,2)_{Cl}$ calculated from the data in MCl media [1981MIL2], [1981SUR/MIL] and MCl_2 media [1982SUR/MIL] are in good agreement. They are used in the present review, together with the data of [1968HIE/SIL] in 3 M NaCl, for the selection of data for the complex $\mathrm{Th_2(OH)_3^{5+}}$.

- *Calorimetric measurements in [1981MIL2]*

Calorimetric measurements were performed as back-titrations of hydrolysed Th(IV) equilibrium solutions in 0.5−3 M NaCl, 3 M LiCl and 3 M KCl with HCl standard solutions [1981MIL2]. No details are reported, which is unfortunate as it makes it impossible to estimate the accuracy of the results obtained. The following information is missing: the concentration of the HCl titrant and its enthalpy of dilution; the relative amounts of $\mathrm{Th_2(OH)_3^{5+}}$ and $\mathrm{Th_2(OH)_2^{6+}}$, where the first complex is a minor species, a fact that will strongly affect the accuracy of the corresponding molar enthalpy of reaction. It is not clear from the information given if the full-drawn curves in Figures 4 and 5 of [1981MIL2] have been calculated using the data in Table A-53, or not. The results

([1981MIL2], Table A-53) are given without uncertainties and the number of digits given is no indication of the accuracy; the error in $\Delta_r H_m$(2,2) is at least 2−3% and much larger in $\Delta_r H_m$(3,2). The enthalpy of reaction is large and for the (2,2) complex of the same order of magnitude as the enthalpy of protonation of OH^-; in view of this it is not surprising that the enthalpy of reaction at a given ionic strength of 3 M varies significantly with the ionic medium (NaCl, LiCl and KCl). The enthalpy of protonation of OH^- is −57.5 kJ·mol^{-1} in 1 m NaCl and −56.1 kJ·mol^{-1} in 1 m $NaClO_4$ ([1997GRE/PLY2], p. 418, 420). The ionic strength dependence of this reaction is also significant and varies from −58.5 kJ·mol^{-1} to −57.2 kJ·mol^{-1} between 3 m and 0.5 m NaCl. However, the ionic strength dependence in [1981MIL2] is much larger than expected; a discussion of the ionic strength dependence of reaction enthalpies is given in [1997GRE/PLY2] (see Chapter IX). From the strong dependence of the reaction enthalpies on the chloride concentration, one would expect a larger variation of $\log_{10} {}^*\beta_{n,2}$ than observed, suggesting that the experimental observations may be due to another effect. As indicated above, part of the differences may be artefacts due to the neglect of the medium-dependent enthalpy of dilution of HCl.

Table A-54: Gibbs energies, enthalpies and entropies of hydrolysis reactions reported in [1981MIL2].

Medium	$\Delta_r G_m$ (kJ·mol^{-1})	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})
$2Th^{4+} + 2H_2O(l) \rightleftharpoons Th_2(OH)_2^{6+} + 2H^+$			
0.5 M NaCl	27.9	86.7	197.3
1.0 M NaCl	27.8	87.0	198.7
1.5 M NaCl	28.2	98.3	235.2
2.0 M NaCl	28.6	109.8	272.5
2.5 M NaCl	28.8	110.3	273.5
3.0 M NaCl	28.9	119.0	302.3
3.0 M LiCl	29.8	133.6	348.3
3.0 M KCl	28.7	101.9	245.6
$2Th^{4+} + 3H_2O(l) \rightleftharpoons Th_2(OH)_3^{5+} + 3H^+$			
0.5 M NaCl	44.4	90.7	155.4
1.0 M NaCl	45.2	76.8	106.0
1.5 M NaCl	45.7	60.1	48.3
2.0 M NaCl	46.2	45.3	− 3.0
2.5 M NaCl	46.3	33.3	− 43.6
3.0 M NaCl	46.9	21.2	− 86.2
3.0 M LiCl	47.2	23.1	− 80.9
3.0 M KCl	46.5	38.1	− 28.2

In 1 M NaCl, the enthalpy of reaction for the formation of $Th_2(OH)_2^{6+}$ is in fair agreement with the value in 1 M $NaClO_4$ given in [1965BAE/MEY], although the entropy of reaction differs significantly. In general, data obtained by calorimetry are more precise than those from the temperature variation of equilibrium constants [1965BAE/MEY], [1976BAE/MES], [2000EKB/ALB], but in view of the criticism given above this review does not accept the reported enthalpy and entropy values.

[1981SMI/MES]

The solubility of $ThF_4(s)$ has been measured as a function of temperature and the concentration of HF in 4, 8 and 13 M nitric acid. The experimental data have been used to determine equilibrium constants for the complexes ThF_n^{4-n} , $n = 1-4$, and the solubility product of $ThF_4(s)$. The experimental method is described in detail and the primary experimental data are included. The composition of solid phase has been determined using elemental analysis and the solid has also been characterised using X-ray diffraction. However, the authors were not able to determine the state of hydration for the freshly formed $ThF_4(s)$ that was amorphous and gave a poor X-ray powder pattern; the solid may thus be any of the known stable hydrates, $ThF_4{\cdot}2.5\text{-}3.0\,H_2O$, $ThF_4{\cdot}0.5\text{-}2.5\,H_2O$ and $ThF_4{\cdot}0.25\,H_2O$. The analysis of the experimental data is satisfactory, but the authors point out that the least-squares analysis is complicated by the large number of parameters, in combination with the scattering of the solubility data. The key problem is that the concentration of free HF has not been measured directly and therefore has to be determined from the mass balance. Therefore, there is a strong correlation between [HF] and the equilibrium constants. However, the agreement between the deduced equilibrium constants obtained in [1981SMI/MES] and previous studies using different experimental methods is good and this review therefore accepts the proposed constants given in Table A-55.

The stepwise equilibrium constants, $\log_{10}{}^{*}K_n$, for the reactions:

$$ThF_{n-1}^{5-n} + HF(aq) \rightleftharpoons ThF_n^{4-n} + H^+ \qquad n = 1-4$$

are obtained from the data given in Table A-55 and are listed below for the data at 25°C in 4 M and 8 M HNO_3 that are the most accurate; the errors are estimated by this review.

$$4\text{ M HNO}_3\text{:}\quad \log_{10}{}^{*}K_1 = (3.8 \pm 0.4);\ \log_{10}{}^{*}K_2 = (3.0 \pm 0.4)$$
$$\log_{10}{}^{*}K_3 = (2.2 \pm 0.4);\ \log_{10}{}^{*}K_4 = (1.4 \pm 0.4);$$

$$8\text{ M HNO}_3\text{:}\quad \log_{10}{}^{*}K_1 = (3.2 \pm 0.4);\ \log_{10}{}^{*}K_2 = (2.7 \pm 0.4)$$
$$\log_{10}{}^{*}K_3 = (2.3 \pm 0.4);\ \log_{10}{}^{*}K_4 = (1.9 \pm 0.4).$$

For complexes of the type discussed here one often finds a regular decrease in the stepwise equilibrium constants. In this respect the data (based on the least-squares method) look satisfactory. However, the data in 8 M and 13 M HNO_3 have not been used in the selection of equilibrium constants because of the high ionic strength.

Table A-55: Concentration equilibrium constants[a] reported in [1981SMI/MES].

t (°C)	Reaction	$\log_{10}{}^*K$ 4 M HNO_3	$\log_{10}{}^*K$ 8 M HNO_3	$\log_{10}{}^*K$ 13 M HNO_3
	$ThF_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq)$			
25		– 16.25 ± 0.4	– 15.60 ± 0.4	– 15.9 ± 0.7
50		– 15.06 ± 0.3	– 14.00 ± 0.3	– 16.7 ± 0.1
100		– 14.3 ± 0.7	– 14.36 ± 0.55	– 16.15 ± 0.6
	$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$			
25		3.8	3.2	2.7
50		3.7	2.9	2.8
100		3.3	2.9	2.7
	$ThF^{3+} + HF(aq) \rightleftharpoons ThF_2^{2+} + H^+$			
25		3.0	2.7	2.7
50		2.9	2.5	3.0
100		2.7	2.6	2.8
	$ThF_2^{2+} + HF(aq) \rightleftharpoons ThF_3^{+} + H^+$			
25		2.2	2.3	2.8
50		2.0	2.1	3.3
100		2.2	2.4	3.0
	$ThF_3^{+} + HF(aq) \rightleftharpoons ThF_4(aq) + H^+$			
25		1.4	1.9	2.8
50		1.2	1.7	3.5
100		1.6	2.2	3.1

a: Values of the solubility products are based on least-squares analyses and the other constants on the constant step-decrement model reported in their Tables 4 and 7, respectively.

Smith *et al.* have also interpreted their data using models with a smaller number of parameters, one parameter relating the complex formation constant in solution to the solubility product of the solid phase, one parameter describing the ratio between two consecutive stepwise equilibrium constants and one parameter describing an assumed regular decrease in this ratio between the stepwise equilibrium constants (Table A-55). Methods like these have been used in studies where the scattering in the experimental data and the number of parameters cannot provide a unique chemical model. In general, Smith *et al.* report a reasonable agreement between the constants calculated with least-squares and the step-decrement methods. The scatter of the experimental data and the uncertainty of the equilibrium constants are so large that the data at different temperature cannot be used to deduce the enthalpy and entropy of reaction.

Because of the very high ionic strengths and the large degree of scatter in the data, it is not possible to precisely determine simultaneously the values of formation constants and the solubility product for ThF_4(cr, hyd) from these data. This review has developed an aqueous phase model in the fluoride system (Table VIII-7) independent of the data in [1981SMI/MES]. These aqueous phase data were used to calculate the solubility products for ThF_4(cr, hyd) with the NONLINT-SIT code and to verify the reliability of the aqueous phase model. Only the data for 4 and 8 M (4.557 and 10.75 m) nitric acid at 25°C and 50°C were reanalysed. In order to do so, the molarities of different elements reported by the authors were converted to molalities. The SIT ion-interaction parameters $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-)$, $\varepsilon(\mathrm{ThF}^{3+},\mathrm{NO}_3^-)$, $\varepsilon(\mathrm{ThF}_2^{2+},\mathrm{NO}_3^-)$, and $\varepsilon(\mathrm{ThF}_3^{+},\mathrm{NO}_3^-)$ used in these analyses are listed in Table VIII-8. Reanalyses of [1981SMI/MES] data provided $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}/\mathrm{R}T$ values for ThF_4(cr, hyd) of $-(811.372 \pm 2.46)$ at 25°C and $-(811.146 \pm 2.32)$ at 50°C for 4.557 m ionic strength data and of $-(813.058 \pm 4.16)$ at 25°C and $-(813.447 \pm 4.90)$ at 50°C for 10.75 m ionic strength data. The $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}/\mathrm{R}T$ values for ThF_4(cr, hyd) thus determined from the data at I = 4.557 m are very similar to the value $-(811.860 \pm 0.915)$ recommended in this review based on solubility studies [1993FEL/RAI] in relatively dilute electrolytes, 0.0001 to 0.01 M. There is some scatter in the data, but the overall agreement between the experimental and predicted thorium concentrations as a function of F^- indicates that the aqueous phase model and $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}/\mathrm{R}T$ value for ThF_4(cr, hyd) selected in this review are consistent with the data at I = 4.557 m (Figure VIII-2, Table A-56 and Table A-57). Although the standard deviation in $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}/\mathrm{R}T$ value for ThF_4(cr, hyd) based on the data at I = 10.57 m is larger than the standard deviation based on the data at I = 4.557 m and that it is questionable whether the SIT model is applicable to these high ionic strength (10.57 m) solutions, the $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}/\mathrm{R}T$ values for ThF_4(cr, hyd) calculated from these data are still within the range of values recommended in this review and thus lends further credence to the values selected here. The experimental and predicted concentrations for different species are presented in Table A-58 and Table A-59 and are compared in Figure A-28 and Figure A-29.

Table A-56: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 25°C in 4.557 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(811.372 \pm 2.460)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
3.315E-01	8.127E-05	4.101E-06	1.482E-06	2.992E-12	2.948E-09	1.122E-07	4.503E-07	9.163E-07	8.127E-05
3.885E-01	9.644E-05	5.184E-06	1.377E-06	1.495E-12	1.754E-09	7.944E-08	3.791E-07	9.163E-07	9.644E-05
3.965E-01	9.860E-05	5.480E-06	1.365E-06	1.366E-12	1.640E-09	7.597E-08	3.707E-07	9.163E-07	9.860E-05
1.025E-01	2.393E-05	1.124E-05	3.879E-06	4.133E-10	1.181E-07	1.309E-06	1.535E-06	9.163E-07	2.392E-05
6.801E-02	1.576E-05	1.196E-05	6.687E-06	2.208E-09	4.146E-07	3.022E-06	2.332E-06	9.163E-07	1.576E-05
6.186E-02	1.432E-05	1.208E-05	7.703E-06	3.245E-09	5.535E-07	3.663E-06	2.567E-06	9.163E-07	1.431E-05
5.491E-02	1.269E-05	1.230E-05	9.278E-06	5.264E-09	7.954E-07	4.664E-06	2.897E-06	9.163E-07	1.269E-05
2.461E-02	5.634E-06	4.637E-05	4.042E-05	1.363E-07	9.124E-06	2.371E-05	6.530E-06	9.163E-07	5.631E-06
1.139E-02	2.566E-06	1.196E-04	2.184E-04	2.918E-06	9.078E-05	1.097E-04	1.404E-05	9.163E-07	2.619E-06
1.138E-02	2.418E-06	5.195E-04	2.991E-04	4.934E-06	1.346E-04	1.426E-04	1.601E-05	9.163E-07	2.297E-06
1.151E-02	2.194E-06	1.242E-03	5.396E-04	1.283E-05	2.756E-04	2.299E-04	2.033E-05	9.163E-07	1.809E-06
1.151E-02	1.177E-06	4.808E-03	4.096E-03	2.720E-04	2.721E-03	1.058E-03	4.359E-05	9.163E-07	8.443E-07
1.185E-02	5.735E-07	8.556E-03	8.774E-03	8.000E-04	6.105E-03	1.811E-03	5.703E-05	9.163E-07	6.458E-07
1.219E-02	3.343E-07	1.151E-02	1.249E-02	1.306E-03	8.811E-03	2.312E-03	6.441E-05	9.163E-07	5.720E-07
3.144E-02	5.000E-07	2.791E-02	2.747E-02	3.818E-03	1.963E-02	3.935E-03	8.395E-05	9.163E-07	4.399E-07
3.395E-02	2.095E-07	4.181E-02	4.442E-02	7.259E-03	3.166E-02	5.399E-03	9.820E-05	9.163E-07	3.770E-07
7.223E-02	3.580E-07	7.495E-02	7.414E-02	1.428E-02	5.224E-02	7.505E-03	1.155E-04	9.163E-07	3.219E-07
7.941E-02	3.804E-07	8.100E-02	7.947E-02	1.564E-02	5.587E-02	7.842E-03	1.180E-04	9.163E-07	3.152E-07
1.151E-01	4.193E-07	1.151E-01	1.108E-01	2.414E-02	7.684E-02	9.655E-03	1.307E-04	9.163E-07	2.861E-07
1.173E-01	3.839E-07	1.208E-01	1.171E-01	2.596E-02	8.104E-02	9.995E-03	1.329E-04	9.163E-07	2.815E-07
1.208E-01	3.869E-07	1.242E-01	1.203E-01	2.687E-02	8.309E-02	1.016E-02	1.340E-04	9.163E-07	2.795E-07
1.219E-01	9.866E-08	2.279E-01	2.463E-01	6.797E-02	1.625E-01	1.562E-02	1.647E-04	9.163E-07	2.312E-07
2.370E-01	1.651E-07	3.520E-01	3.603E-01	1.109E-01	2.298E-01	1.940E-02	1.823E-04	9.163E-07	2.118E-07
2.746E-01	1.720E-07	4.044E-01	4.112E-01	1.314E-01	2.587E-01	2.088E-02	1.886E-04	9.163E-07	2.059E-07
3.008E-01	1.958E-07	4.192E-01	4.210E-01	1.354E-01	2.642E-01	2.116E-02	1.897E-04	9.163E-07	2.049E-07
2.165E-01	7.923E-08	4.979E-01	5.384E-01	1.855E-01	3.285E-01	2.417E-02	2.016E-04	9.163E-07	1.952E-07
3.976E-01	1.662E-07	6.175E-01	6.252E-01	2.244E-01	3.744E-01	2.616E-02	2.088E-04	9.163E-07	1.899E-07
4.272E-01	1.353E-07	7.542E-01	7.751E-01	2.948E-01	4.508E-01	2.923E-02	2.194E-04	9.163E-07	1.831E-07

Table A-57: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 50°C in 4.557 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G_m^o / RT$ value for ThF_4(cr, hyd) of $-(811.146 \pm 2.320)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
7.063×10^{-2}	1.637×10^{-5}	2.165×10^{-5}	7.939×10^{-6}	2.377×10^{-9}	4.638×10^{-7}	3.511×10^{-6}	2.814×10^{-6}	1.148×10^{-6}	1.637×10^{-5}
2.051×10^{-2}	4.664×10^{-6}	1.048×10^{-4}	7.537×10^{-5}	3.679×10^{-7}	2.033×10^{-5}	4.361×10^{-5}	9.913×10^{-6}	1.148×10^{-6}	4.649×10^{-6}
1.481×10^{-2}	3.234×10^{-6}	4.101×10^{-4}	1.825×10^{-4}	1.826×10^{-6}	6.759×10^{-5}	9.714×10^{-5}	1.479×10^{-5}	1.148×10^{-6}	3.116×10^{-6}
1.709×10^{-2}	2.008×10^{-6}	5.468×10^{-3}	3.327×10^{-3}	1.818×10^{-4}	2.129×10^{-3}	9.682×10^{-4}	4.670×10^{-5}	1.148×10^{-6}	9.876×10^{-7}
3.646×10^{-2}	4.020×10^{-7}	3.532×10^{-2}	3.565×10^{-2}	5.024×10^{-3}	2.548×10^{-2}	5.042×10^{-3}	1.063×10^{-4}	1.148×10^{-6}	4.358×10^{-7}
5.696×10^{-2}	3.673×10^{-7}	5.810×10^{-2}	5.819×10^{-2}	9.676×10^{-3}	4.144×10^{-2}	6.951×10^{-3}	1.246×10^{-4}	1.148×10^{-6}	3.730×10^{-7}
1.253×10^{-1}	2.606×10^{-7}	1.481×10^{-1}	1.492×10^{-1}	3.346×10^{-2}	1.030×10^{-1}	1.259×10^{-2}	1.667×10^{-4}	1.148×10^{-6}	2.826×10^{-7}
1.253×10^{-1}	1.587×10^{-7}	1.823×10^{-1}	1.913×10^{-1}	4.623×10^{-2}	1.302×10^{-1}	1.464×10^{-2}	1.792×10^{-4}	1.148×10^{-6}	2.644×10^{-7}
2.051×10^{-1}	1.862×10^{-7}	2.848×10^{-1}	2.915×10^{-1}	7.991×10^{-2}	1.926×10^{-1}	1.876×10^{-2}	2.015×10^{-4}	1.148×10^{-6}	2.380×10^{-7}
3.418×10^{-1}	1.329×10^{-7}	5.924×10^{-1}	6.159×10^{-1}	2.098×10^{-1}	3.775×10^{-1}	2.840×10^{-2}	2.438×10^{-4}	1.148×10^{-6}	2.036×10^{-7}

Table A-58: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 25°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(813.06 \pm 4.160)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
5.121×10^{-1}	2.134×10^{-5}	1.357×10^{-5}	5.756×10^{-7}	4.234×10^{-12}	1.656×10^{-9}	4.946×10^{-8}	3.548×10^{-7}	1.697×10^{-7}	2.134×10^{-5}
4.005×10^{-1}	1.652×10^{-5}	1.357×10^{-5}	7.146×10^{-7}	1.186×10^{-11}	3.583×10^{-9}	8.268×10^{-8}	4.586×10^{-7}	1.697×10^{-7}	1.652×10^{-5}
1.212×10^{-1}	4.871×10^{-6}	3.588×10^{-5}	2.826×10^{-6}	1.593×10^{-9}	1.411×10^{-7}	9.554×10^{-7}	1.558×10^{-6}	1.697×10^{-7}	4.869×10^{-6}
7.701×10^{-2}	3.080×10^{-6}	6.061×10^{-5}	5.602×10^{-6}	1.003×10^{-8}	5.603×10^{-7}	2.396×10^{-6}	2.466×10^{-6}	1.697×10^{-7}	3.076×10^{-6}
5.484×10^{-2}	2.182×10^{-6}	1.226×10^{-4}	1.009×10^{-5}	4.024×10^{-8}	1.588×10^{-6}	4.798×10^{-6}	3.490×10^{-6}	1.697×10^{-7}	2.174×10^{-6}
1.344×10^{-2}	4.849×10^{-7}	8.978×10^{-4}	3.696×10^{-4}	2.605×10^{-5}	2.038×10^{-4}	1.220×10^{-4}	1.760×10^{-5}	1.697×10^{-7}	4.312×10^{-7}
1.357×10^{-2}	4.597×10^{-7}	1.465×10^{-3}	5.647×10^{-4}	4.903×10^{-5}	3.275×10^{-4}	1.674×10^{-4}	2.061×10^{-5}	1.697×10^{-7}	3.682×10^{-7}
1.357×10^{-2}	1.614×10^{-7}	1.012×10^{-2}	9.754×10^{-3}	2.423×10^{-3}	6.100×10^{-3}	1.176×10^{-3}	5.462×10^{-5}	1.697×10^{-7}	1.390×10^{-7}
1.384×10^{-2}	1.109×10^{-7}	1.384×10^{-2}	1.412×10^{-2}	3.883×10^{-3}	8.685×10^{-3}	1.488×10^{-3}	6.143×10^{-5}	1.697×10^{-7}	1.237×10^{-7}
1.452×10^{-2}	3.180×10^{-8}	3.521×10^{-2}	3.923×10^{-2}	1.385×10^{-2}	2.249×10^{-2}	2.802×10^{-3}	8.424×10^{-5}	1.697×10^{-7}	9.030×10^{-8}
2.930×10^{-2}	5.918×10^{-8}	4.825×10^{-2}	5.018×10^{-2}	1.870×10^{-2}	2.814×10^{-2}	3.251×10^{-3}	9.071×10^{-5}	1.697×10^{-7}	8.391×10^{-8}
3.521×10^{-2}	7.628×10^{-8}	5.027×10^{-2}	5.081×10^{-2}	1.898×10^{-2}	2.846×10^{-2}	3.275×10^{-3}	9.105×10^{-5}	1.697×10^{-7}	8.360×10^{-8}
3.857×10^{-2}	5.502×10^{-8}	6.747×10^{-2}	6.983×10^{-2}	2.787×10^{-2}	3.790×10^{-2}	3.960×10^{-3}	1.001×10^{-4}	1.697×10^{-7}	7.616×10^{-8}
4.704×10^{-2}	4.407×10^{-8}	9.583×10^{-2}	1.001×10^{-1}	4.287×10^{-2}	5.220×10^{-2}	4.893×10^{-3}	1.111×10^{-4}	1.697×10^{-7}	6.870×10^{-8}
5.578×10^{-2}	3.602×10^{-8}	1.314×10^{-1}	1.382×10^{-1}	6.287×10^{-2}	6.933×10^{-2}	5.899×10^{-3}	1.219×10^{-4}	1.697×10^{-7}	6.278×10^{-8}
7.903×10^{-2}	5.753×10^{-8}	1.384×10^{-1}	1.396×10^{-1}	6.359×10^{-2}	6.992×10^{-2}	5.932×10^{-3}	1.222×10^{-4}	1.697×10^{-7}	6.261×10^{-8}
8.091×10^{-2}	5.708×10^{-8}	1.425×10^{-1}	1.437×10^{-1}	6.582×10^{-2}	7.172×10^{-2}	6.032×10^{-3}	1.232×10^{-4}	1.697×10^{-7}	6.211×10^{-8}
1.371×10^{-1}	2.334×10^{-8}	4.731×10^{-1}	4.966×10^{-1}	2.787×10^{-1}	2.058×10^{-1}	1.195×10^{-2}	1.718×10^{-4}	1.697×10^{-7}	4.539×10^{-8}
1.411×10^{-1}	1.725×10^{-8}	6.371×10^{-1}	6.755×10^{-1}	3.965×10^{-1}	2.648×10^{-1}	1.402×10^{-2}	1.853×10^{-4}	1.697×10^{-7}	4.243×10^{-8}

Table A-59: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 50°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(813.45 \pm 4.90)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
7.795×10^{-2}	3.115×10^{-6}	8.602×10^{-5}	3.732×10^{-6}	6.505×10^{-9}	3.675×10^{-7}	1.589×10^{-6}	1.654×10^{-6}	1.150×10^{-7}	3.110×10^{-6}
4.435×10^{-2}	1.717×10^{-6}	6.586×10^{-4}	1.120×10^{-5}	7.892×10^{-8}	2.388×10^{-6}	5.531×10^{-6}	3.085×10^{-6}	1.150×10^{-7}	1.667×10^{-6}
1.747×10^{-2}	5.394×10^{-7}	2.688×10^{-3}	5.329×10^{-4}	5.384×10^{-5}	3.188×10^{-4}	1.444×10^{-4}	1.576×10^{-5}	1.150×10^{-7}	3.263×10^{-7}
3.494×10^{-2}	5.021×10^{-8}	6.451×10^{-2}	6.663×10^{-2}	2.839×10^{-2}	3.487×10^{-2}	3.291×10^{-3}	7.509×10^{-5}	1.150×10^{-7}	6.877×10^{-8}
3.763×10^{-2}	4.592×10^{-8}	7.392×10^{-2}	7.663×10^{-2}	3.352×10^{-2}	3.946×10^{-2}	3.571×10^{-3}	7.821×10^{-5}	1.150×10^{-7}	6.607×10^{-8}
6.586×10^{-2}	3.086×10^{-8}	1.747×10^{-1}	1.825×10^{-1}	9.272×10^{-2}	8.384×10^{-2}	5.865×10^{-3}	9.991×10^{-5}	1.150×10^{-7}	5.205×10^{-8}
9.139×10^{-2}	2.938×10^{-8}	2.554×10^{-1}	2.653×10^{-1}	1.429×10^{-1}	1.151×10^{-1}	7.212×10^{-3}	1.105×10^{-4}	1.150×10^{-7}	4.727×10^{-8}
1.089×10^{-1}	2.497×10^{-8}	3.494×10^{-1}	3.644×10^{-1}	2.056×10^{-1}	1.501×10^{-1}	8.559×10^{-3}	1.201×10^{-4}	1.150×10^{-7}	4.374×10^{-8}
1.331×10^{-1}	2.341×10^{-8}	4.570×10^{-1}	4.758×10^{-1}	2.788×10^{-1}	1.870×10^{-1}	9.854×10^{-3}	1.285×10^{-4}	1.150×10^{-7}	4.112×10^{-8}

Figure A-28: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 25°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(813.06 \pm 4.16)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

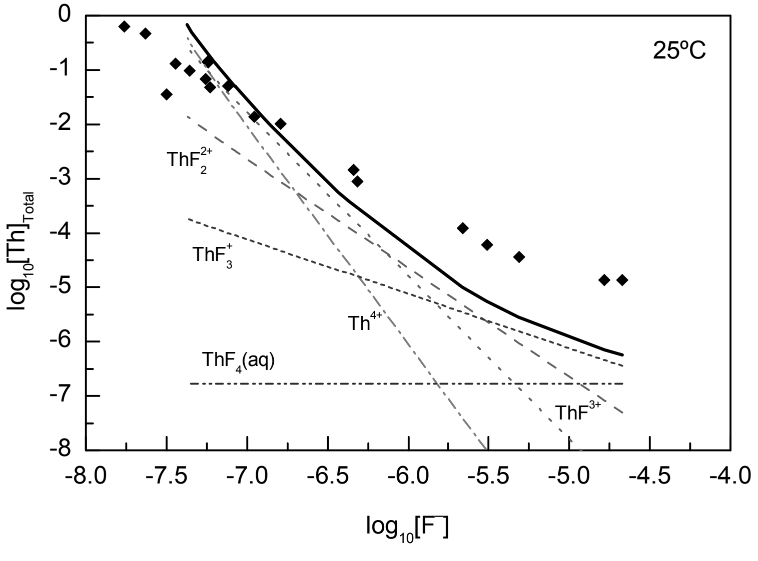
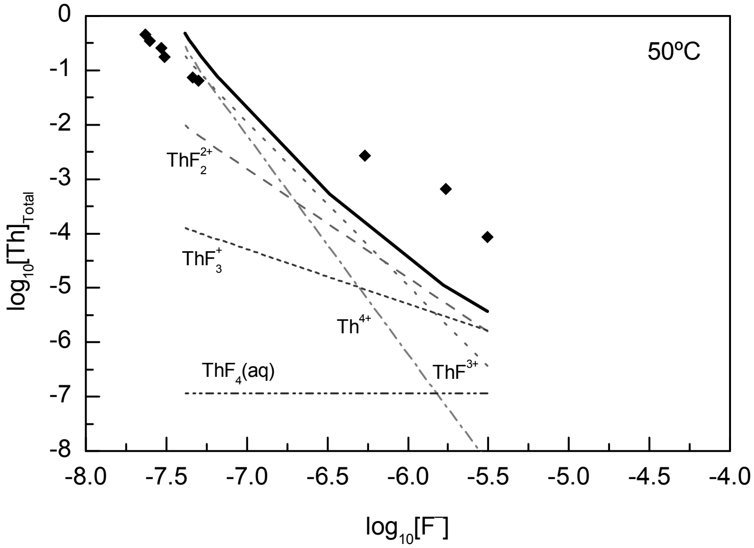


Figure A-29: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 50°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(813.45 \pm 4.90)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.



[1981SUR/MIL]

Milić [1981MIL2] and Šuranji and Milić [1981SUR/MIL], [1982SUR/MIL] investigated the hydrolytic behaviour of thorium(IV) in various aqueous chloride media at 25°C. These papers are discussed together, *cf.* Appendix A review of [1981MIL2].

[1982BOR/BOR2]

This study was centred on the determination of the enthalpies of formation of the various compounds found in the Th-Bi system. X-ray data and metallographic analyses were also reported.

Thorium metal and bismuth powders of nominal purities 99.8% and 99.999%, respectively, were used and the various alloys were prepared by induction melting the required amounts of thorium and bismuth in tantalum crucibles. Handling the samples and welding of the crucibles were conducted under argon atmosphere.

As shown in Table X-6, Section X.5.1 the reported structures and lattice parameters of the compounds Th_3Bi_4 and $ThBi_2$ confirmed earlier literature results; in addition, new structural data were given for the compounds Th_5Bi_3 and ThBi. However, the authors noted that the ThBi(cr) may be metastable, and that the Th_5Bi_3(cr) phase may be stabilised by minor impurities, like some other phases with this structure.

Use was made of an isoperibol aneroid calorimeter assembly in which the alloys are prepared directly. The instrument had been described previously by the same group [1974CAP/FER]; its performance has been checked with alloy systems of which the enthalpies of formation were already reported in the literature. Results of the measurement at 300 K of the enthalpy of formation of 13 Th-Bi alloys ranging from$Th_{0.2}Bi_{0.8}$ to $Th_{0.75}Bi_{0.25}$ were reported. The reaction was found to be incomplete in the measurements of five further alloys. The following enthalpies of formation, consistent with the formation of the four compounds given above, were derived: $\Delta_f H_m$ (Th_5Bi_3, cr, 298.15 K) = $-(532.2 \pm 16.7)$ kJ·mol^{-1}, $\Delta_f H_m$ (ThBi, cr, 298.15 K) = $-(162.3 \pm 4.2)$ kJ·mol^{-1}, $\Delta_f H_m$ (Th_3Bi_4, cr, 298.15 K) = $-(597.5 \pm 14.6)$ kJ·mol^{-1}, and $\Delta_f H_m$ ($ThBi_2$, cr, 298.15 K) = $-(207.1 \pm 6.3)$ kJ·mol^{-1}. The uncertainty limits reported by the authors appear in line with the performances of the calorimetric assembly. Using their results and earlier available data, the authors propose a tentative phase diagram for the Th-Bi system.

[1982FIN]

The author used a three parameter fit of the enthalpy up to the λ-transition, taken to be at 2950 K from the work of [1981FIS/FIN]. This equation is based on lattice (Einstein) and thermal expansion (plus anharmonic) contributions:

$$H_m(T) - H_m^\circ(298.15\,\text{K}) = C_1\,\theta / (e^{\,\theta/T} - 1) + C_2 T^2 + \text{constant}$$

with $C_1 = 68.654$ J·K^{-1}·mol^{-1}, $\theta = 408.14$ K and $C_2 = 4.8174 \times 10^{-3}$ J·K^{-2}·mol^{-1} and the constant (-9988 J·mol^{-1}) is determined from $H_m(T) - H_m^\circ(298.15\,\text{K}) = 0$.

This expression fits the enthalpy and heat capacity data very well, and merges with the low temperature heat capacity data of [1953OSB/WES], since a constraint on $C_{p,m}^\circ$ at 298.15 K was imposed in the fitting. These data agree very well with those selected by this review. The data at higher temperatures (> 2900 K) are not entirely consistent with the enthalpy calculated from the $C_{p,m}^\circ$ measurements of [1996RON/HIE], who showed that the transition is second order, with a peak in the heat capacity at (3090 ± 10) K, as discussed in Section VII.1.2.

[1982JOL/THO]

The authors have used the known structure data and discuss the effect of the bidentate coordination of the carbonate ligand on the splitting of the ν_3(E) vibration frequency. There are no thermodynamic data in this study.

[1982MIL/SUR2]

This potentiometric study of the hydrolysis of Th^{4+} in $NaNO_3$ solutions provides all experimental details and follows the approach of the Sillén school both with regards to experimental technique and data analysis. The experiments have been made at 25.0°C using six different total concentrations of Th, from 2.5 to 100 mM. The $-\log_{10}[\mathrm{H}^+]$ range investigated was 1.5 to 3.5 and the corresponding $\bar{n}_{\mathrm{OH}}$ values vary from 0 to 0.35−0.40. The reversibility of the titrations were tested at $[\mathrm{Th}]_{\mathrm{tot}}$ = 2.5 and 10 mM. Three different complexes were proposed, $\mathrm{Th}_2(\mathrm{OH})_2^{6+}$, $\mathrm{Th}_3(\mathrm{OH})_5^{7+}$ and $\mathrm{Th}_6(\mathrm{OH})_{15}^{9+}$; their equilibrium constants, $\log_{10} {}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$, were determined at six different total concentrations of the $\mathrm{NaNO_3}$ ionic medium as shown in Table A-60. The large uncertainty in the determination of the equilibrium constant for the (15,6) complex is due to the small maximum value of $\bar{n}_{\mathrm{OH}}$.

Table A-60: Equilibrium constants $\log_{10} {}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ ± 3σ for the hydrolysis reactions of Th^{4+} in $\mathrm{(Na)NO_3}$ ionic media. For some of the values of $\log_{10} {}^*\beta_{15,6}$ only a range of values could be given; the uncertainty of these values is estimated to 0.5 by this review.

$\mathrm{(Na)NO_3}$ medium (M)	$-\log_{10} {}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}) \pm 3\,\sigma$		
	$\mathrm{Th}_2(\mathrm{OH})_2^{6+}$	$\mathrm{Th}_3(\mathrm{OH})_5^{7+}$	$\mathrm{Th}_6(\mathrm{OH})_{15}^{9+}$
0.5	5.06 ± 0.07	12.59 ± 0.12	38.06 ± 0.23
1.0	5.08 ± 0.06	13.04 ± 0.15	39.56 − 39.41
1.5	5.14 ± 0.05	13.30 ± 0.16	40.47 − 40.13
2.0	5.16 ± 0.04	13.61 ± 0.16	41.10 − 40.83
2.5	5.18 ± 0.03	13.79 ± 0.15	41.77 − 41.42
3.0	5.19 ± 0.02	14.23 ± 0.17	42.32 ± 0.23

The authors have described the variation of the equilibrium constants in the different ionic media using a linear correlation between $-\log_{10} {}^*\beta_{n,m}$ and a "medium factor" that is not defined but that depends on the ionic medium concentration and the hydration energy of its ions. They have used the same method to compare them with the data in 3 M $\mathrm{(Li)NO_3}$, $\mathrm{(Na)NO_3}$, $\mathrm{(K)NO_3}$ and 4 M $\mathrm{(Na)NO_3}$. This review prefers to analyse the data using the specific ion interaction theory. Use of solely of the results of [1982MIL/SUR2] in 0.5−3.0 M $\mathrm{NaNO_3}$ gives the following values:

$$\log_{10} {}^*\beta^{\circ}_{2,2} = -(6.13 \pm 0.10) \qquad \Delta\varepsilon(2,2) = (0.18 \pm 0.05)\ \mathrm{kg{\cdot}mol^{-1}},$$

$$\log_{10} {}^*\beta^{\circ}_{5,3} = -(13.5 \pm 0.2) \qquad \Delta\varepsilon(5,3) = (0.57 \pm 0.07)\ \mathrm{kg{\cdot}mol^{-1}},$$

$$\log_{10} {}^*\beta^{\circ}_{15,6} = -(37.4 \pm 0.6) \qquad \Delta\varepsilon(15,6) = (1.37 \pm 0.17)\ \mathrm{kg{\cdot}mol^{-1}},$$

The value of $\log_{10} {}^*\beta^{\circ}_{2,2}$ in 4 M $\mathrm{(Na)NO_3}$ calculated by assuming that the SIT can be used at this high ionic strength is equal to − 5.56, in good agreement with the experimental value in [1968DAN/MAG].

[1982SUR/MIL]

Milić [1981MIL2] and Šuranji and Milić [1981SUR/MIL], [1982SUR/MIL] investigated the hydrolytic behaviour of thorium(IV) in various chloride media at 25°C. These papers are discussed together, *cf.* Appendix A review of [1981MIL2].

[1982WAG/EVA]

This is a comprehensive compilation of thermodynamic data that has been supplemented by an erratum [1989COX/WAG]. The present comments on this publication pertain only to the thorium sulphate system. Wagman *et al.* [1982WAG/EVA] report $\Delta_f G_m^o$ for the complexes $ThSO_4^{2+}$, $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$ and for $Th(SO_4)_2(cr)$. These data along with other data presented in this compilation provide 5.44, 10.46, 8.44, respectively, for the $\log_{10} \beta^o$ values of equilibrium constants for the following reactions:

$$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+}$$

$$Th^{4+} + 3SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$$

$$Th^{4+} + 4SO_4^{2-} \rightleftharpoons Th(SO_4)_4^{4-}$$

The reported values also provide a $\log_{10} K^o$ value of -9.89 for the following reaction:

$$Th(SO_4)_2(cr) + SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$$

The exact origin of these data is not known, but the most likely source of the data for $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$ is the solvent extraction study of [1963ALL/MCD] conducted at relatively concentrated Na_2SO_4 solutions of variable molality. It is difficult to extrapolate values for highly charged species from concentrated electrolytes without the use of proper models for concentrated electrolytes; in fact when electrolyte models (Pitzer and SIT, see [1992FEL/RAI] and this review) suited for concentrated solutions are used, the data in [1963ALL/MCD] are very well described if the $Th(SO_4)_4^{4-}$ species is omitted from the model (see Figure IX-2).

Most of the available studies on this system show that the species $Th(SO_4)_2(aq)$ is important (see Sections IX.1.3.2.1 and IX.1.3.3), but this species was apparently not included in the assessment by [1982WAG/EVA].

Felmy and Rai [1992FEL/RAI] point out that the calculated solubility of $Th(SO_4)_2(cr)$ based on the thermodynamic data quoted in [1982WAG/EVA] are many orders of magnitude lower than those based on experimental data they quote, indicating serious errors in the data reported in [1982WAG/EVA]. For these reasons, the thermodynamic data reported in this compilation are not accepted by this review.

[1983BRO/ELL]

This potentiometric study has been made at 25°C in a 0.10 M KNO_3 ionic medium. The experimental procedure is only briefly described, but based on the previous publications of these authors we assume that it is satisfactory. Four different total concentrations of Th(IV) have been used, 0.196, 0.490, 0.980 and 1.960 mM in the $-\log_{10}[H^+]$ range 3.14−4.03 covering $\bar{n}_{OH}$ up to 2.5. The authors have analysed the data using MINIQUAD, a least-squares program that allows independent minimisation of two experimental quantities. The experimental data result in the following species and equilibrium constants:

$$\log_{10} {}^*\beta_{1,1} = -(2.98 \pm 0.01)$$
$$\log_{10} {}^*\beta_{12,4} = -(30.55 \pm 0.03)$$
$$\log_{10} {}^*\beta_{15,6} = -(34.41 \pm 0.03).$$

They have also tested a number of the species proposed by Hietanen and Sillén [1964HIE/SIL], [1968HIE/SIL], and by Baes *et al.* [1965BAE/MEY], [1976BAE/MES] and find that they do not improve the chemical model. There are surprisingly large differences between the chemical model proposed in this study and those in previous investigations and the authors suggest that the low ionic strength may be one possible reason for this. This review accepts this suggestion because there is no evidence for flaws in the experimental procedures and data analysis. We can test this assumption by making a speciation calculation at ionic strength 0.1 M using the SIT and the equilibrium constant for $Th_2(OH)_2^{6+}$ from [1982MIL/SUR2]. The result is that $Th_2(OH)_2^{6+}$ is *not* present in significant amounts in the test solutions used by Brown and Ellis. There is thus no contradiction between their experimental results and those of previous investigations claiming the presence of $Th_2(OH)_2^{6+}$.

Their equilibrium constant $\log_{10} {}^*\beta_{1,1} = -(2.98 \pm 0.01)$ differs considerably from the values proposed by [1954KRA/HOL] and [1965BAE/MEY]; it is also inconsistent with that suggested by [1968HIE/SIL] but compatible with the value in [2000EKB/ALB]. We can recalculate the equilibrium constant for the (15,6) complex in 0.1 M KNO_3 to 3 M $NaNO_3$ by using SIT and the value of $\Delta\varepsilon(15,6) = (1.4 \pm 0.2)$ $kg\cdot mol^{-1}$ from [1982MIL/SUR2]; we obtain $\log_{10} {}^*\beta_{15,6} = -(39.2 \pm 0.7)$, in poor agreement with the value $\log_{10} {}^*\beta_{15,6} = -(42.32 \pm 0.23)$ from [1982MIL/SUR2].

[1984AMO/BLA2]

The heat capacities of the non-magnetic oxychalcogenides ThOS(cr) and ThOSe(cr) and of the isomorphous antiferromagnetic UOS(cr) and UOSe(cr) were measured from *ca.* 5 to *ca.* 300 K. The samples were prepared by mixing stoichiometric amounts of the dioxides and disulphides and annealed *in vacuo* in silica tubes at 1273 K for three days. X-ray diffraction analysis of the thorium compounds showed the expected PbFCl structure. For ThOS, a weak extra line due to ThO_2 was detected, and for ThOSe, several non-identified very weak extra lines were found. For the adiabatic heat capacity measurements, the samples were mixed with silver powder, or held in a silver cage, to improve heat conduction. The thorium compounds showed no peaks in the heat capacity curves. The derived values for the heat capacity and entropy at 298.15 K were $C^{\circ}_{p,\mathrm{m}}$(ThOS, cr, 298.15 K) = (67.25 ± 1.35) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, S°_{m}(ThOS, cr, 298.15 K) = (76.3 ± 1.5) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and $C^{\circ}_{p,\mathrm{m}}$(ThOSe, cr, 298.15 K) = (72.65 ± 1.50) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, S°_{m}(ThOSe, cr, 298.15 K) = (93.5 ± 1.9) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. By a comparison of the data for the thorium and uranium compounds, values of the entropy of ordering (close to $R{\cdot}\ln 2$) and Schottky contributions to the heat capacity were calculated for the uranium compounds.

[1984EDV/LAG]

Detailed spectral analysis gave the molecular constants for two new excited states of ThO(g). A concise table is given of the 16 excited states of ThO(g) known at that time.

[1984NAK/ZIM]

The hydrolysis of Th(IV) has been investigated at 25°C in 0.50 M KNO_3 using liquid-liquid extraction technique over the pH range 1.5 to 3.8. Tri-n-butyl phosphate (30 vol.% TBP in dodecane) is used as the extractant; the total concentration of Th(IV) was 10 mM. Under the experimental conditions of this study, neither the extraction of Th nor the co-extraction of HNO_3 has a significant effect on the free TBP concentration in the organic phase. The experiments appear well conducted, but there are only eight experimental points, of which three have been used to determine the equilibrium constant $\log_{10}{}^{*}\beta_{1,1} = -(3.28 \pm 0.1)$ for the formation of $Th(OH)^{3+}$ in the reaction:

$$Th^{4+} + H_2O(l) \rightleftharpoons Th(OH)^{3+} + H^{+}.$$

The authors assume that the concentration of polynuclear complexes can be neglected; the following speciation diagram (Figure A-30) demonstrates that this is a reasonable approximation when the hydrogen ion concentration is higher than 5 mM. The uncertainty in $\log_{10}{}^{*}\beta_{1,1}$ has been estimated by this review.

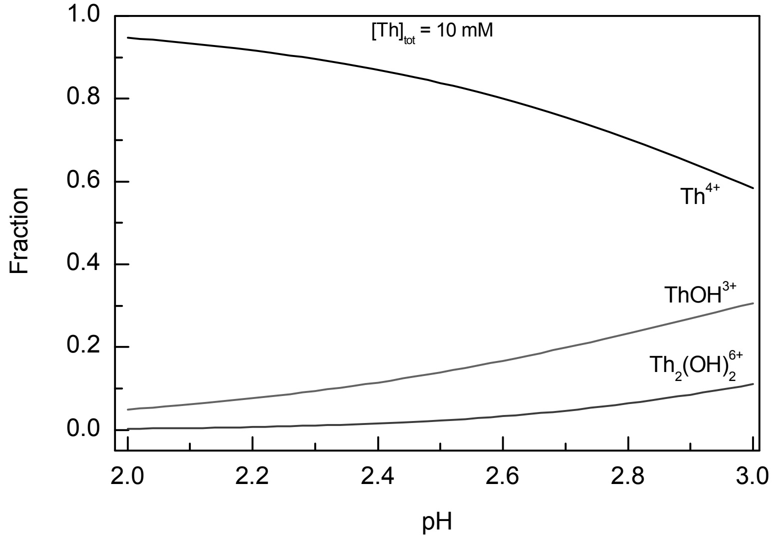
[1985EDV/LAG]

Detailed spectral analysis gave the molecular constants for three new excited states of ThO(g), at 19050, 20062 and 24036 $\mathrm{cm^{-1}}$ which have been included in the calculation of the thermal function (*cf.* [1985EDV/LAG2] and subsequent papers by Edvinsson and colleagues).

[1985EDV/LAG2]

A new low-lying excited state designated Q was found in ThO(g). Analyses of transitions from previously known excited states to this Q state have made it possible to accurately relate the G, H, O, and P states to the ground state. A concise table giving the 17 excited states of ThO(g) known at that time, supplemented by later studies, is the basis for the calculation of the thermal functions of ThO(g).

Figure A-30: Speciation diagram for the Th(IV)-water system in 0.5 M KNO_3 and 25°C.



[1985LIV/MUS]

The paper is a careful Raman spectroscopic study of the complex formation in the Th(IV)-thiocyanate system. The experiments have been made in a mixed SCN^-/ClO_4^- ionic medium where the ionic strength varies. The total concentration of Th(IV) is high, the paper referring to spectra with concentrations 0.275 and 0.50 M. It is not clear from the paper how many different SCN^- concentrations were used to determine the four equilibrium constants reported; the highest concentration mentioned in the paper is 1.46 M. The analysis of the data is straightforward due to the fairly large changes in the ν(C−S) frequency, from 751 to 812 cm^{-1}, between free and coordinated SCN^-. As the ionic medium is not constant and the paper does not contain information on the composition of the test solutions used, it is not possible to evaluate the reliability of the concentration constant given in [1985LIV/MUS]. This review notes that the difference between the consecutive equilibrium constants reported is surprisingly small. Because of the paucity of experimental detail this review can only conclude that the Raman data provides independent information of complex formation in the Th(IV)-thiocyanate system and in addition that the thiocyanate ligand is coordinated at the nitrogen end, as expected for a hard acceptor like Th^{4+}.

Complex	Equilibrium constant β_n / M^{-n}
$Th(SCN)^{3+}$	4.0 ± 0.6
$Th(SCN)_2^{2+}$	5.0 ± 0.1
$Th(SCN)_3^{+}$	5.4 ± 0.1
$Th(SCN)_4$	1.4 ± 0.1

[1986DAV/TOR2]

Davydov and Toropov [1986DAV/TOR2] point out that there are large discrepancies between the published equilibrium constants for the first mononuclear Th(IV) hydroxide complex $Th(OH)^{3+}$ from potentiometric and solubility studies. For these reasons they used different experimental methods, cation exchange and colorimetry in the pH range 1.0−4.0, to determine ${}^*\beta_{1,1}$ ($Th(OH)^{3+}$) at (20 ± 2)°C and $I = 0.1$ M in both nitrate and perchlorate media. To avoid interference of polynuclear species the studies were performed at low total thorium concentrations of 2×10^{-5} to 1×10^{-4} M. Dialysis studies confirmed the absence of large polynuclear Th(IV) complexes and also that there were no artefacts from sorption of Th(IV) on foreign colloids present in the solutions investigated. The formation of thorium colloids at pH > 4.0, shown by dialysis through a cellophane membrane, did not allow them to extend the studies on hydrolysis at $[Th]_{tot} = 2 \times 10^{-5}$ to 1×10^{-4} M to higher pH. The latter observation is in accord with the equilibrium constants selected in the present review, *i.e.*, colloid formation above the solubility limit of ThO_2(am, hyd).

The cation exchange experiments were performed with KU-2 cation exchange resin (equilibration time: 7 days) in HNO_3-$NaNO_3$ solutions, the colorimetric studies with Arsenazo III in both HNO_3-$NaNO_3$ and $HClO_4$-$NaClO_4$ media and with Thoron I in HNO_3-$NaNO_3$ solutions. The pH values were adjusted by dilution of the stock solutions with 0.1 M HNO_3 or 0.1 M $HClO_4$ and addition of NH_3 solution and measured with a glass electrode. Details on the electrode calibration are not reported.

Neither the distribution coefficients K_d nor the optical density (absorption) in the colorimetric studies showed noticeable changes in the pH range 1.0−3.0. The observed changes from pH 3.0 to pH 4.0 were ascribed exclusively to the reaction:

$$Th^{4+} + H_2O(l) \rightleftharpoons Th(OH)^{3+} + H^+$$

Assuming that only Th^{4+} (but not $Th(OH)^{3+}$ or other hydrolysis species) is sorbed onto the cation exchange resin material and that only Th^{4+} forms complexes with the organic reagents used in the colorimetric studies, the following conditional equilibrium constants at (20 ± 2)°C are calculated from the colorimetric studies:

${}^*\beta_{1,1} = (3.6 \pm 1.2) \times 10^{-5}\ M^{-1}$	Arsenazo III, $I = 0.1$ M (HNO_3-$NaNO_3$ and $HClO_4$-$NaClO_4$)
${}^*\beta_{1,1} = (5.2 \pm 1.2) \times 10^{-5}\ M^{-1}$	Thoron I, $I = 0.1$ M (HNO_3-$NaNO_3$)

The cation exchange experiment at $I = 0.1$ M (HNO_3-$NaNO_3$) is not explicitly evaluated; however, it is claimed to confirm the colorimetric results. Further series of cation exchange experiments were performed at constant pH values of 1.0, 2.0 and 3.0 and varying $NaNO_3$ concentration. From the slopes of (3.8 ± 0.4) when $\log_{10}K_d$ is plotted against $\log_{10} a_{Na^+}$ in the range −0.3 to −0.6 the authors concluded that the Th^{4+} ion is the predominant aqueous thorium species up to pH 3. A closer look at Figure 2 in [1986DAV/TOR2] shows that the slopes decrease from pH 1 to pH 3. Moreover, it is by no means ascertained that $Th(OH)^{3+}$ or other hydrolysis species are not sorbed onto the cation exchange resin (*cf.* discussion of [1967BER]) and that they do not form complexes with the organic reagents Arsenazo III or Thoron I. This might explain the very low hydrolysis constant obtained by Davydov and Toropov [1986DAV/TOR2]. The mean value, $\log_{10} {}^*\beta_{1,1}$ ($Th(OH)^{3+}$) = −(4.36 ± 0.14) at $I = 0.1$ M and (20 ± 2)°C, corresponding to $\log_{10} {}^*\beta^{\circ}_{1,1} = -(3.7 \pm 0.2)$ if extrapolated to $I = 0$ with the SIT, is 0.7−1.5 $\log_{10}$ units lower than the values from studies accepted by this review. It is not included in the selection of data for thorium hydroxide complexes.

In a later paper of Davydov and Toropov [1992DAV/TOR], the formation of polynuclear Th(IV) hydroxide complexes is studied at total thorium concentrations of $[Th]_{tot} = 2 \times 10^{-4}$ to 1×10^{-2} M at pH 3.0−4.5 in 0.1 M HNO_3-NH_4NO_3 and 0.1 M $HClO_4$-NH_4NO_4 media by means of dialysis, centrifugation and spectrophotometry (colorimetry). The authors report the formation of binuclear hydroxide complexes under these conditions. They did not observe an influence of the background medium, either nitrate or perchlorate.

This later paper of Davydov and Toropov [1992DAV/TOR] seems to be an extension of their earlier study [1986DAV/TOR2] at $[Th]_{tot}$ = to 2×10^{-5} to 1×10^{-4} M and pH = 1.0−4.0 to solutions of higher Th concentrations and pH values up to 4.5. Numerical values of equilibrium constants for polynuclear complexes are not given in [1992DAV/TOR]. No evaluation was possible as only the abstract was available to the reviewers.

[1986FLE/KNA]

The sublimation pressure of ThI_4(cr) was measured by mass-loss Knudsen effusion (617 to 760 K) and mass spectrometry, in separate studies. The latter confirmed that the sublimation of ThI_4 is accompanied by a small (5 − 10%) dissociation to a lower iodide and iodine.

In the effusion measurements, there was a significant effect of orifice size, and their pressures were extrapolated to zero orifice size (but without taking into account the presence of the small amount of iodine in the vapour). Although the authors indicate that the reproducibility of the raw measurements was rather poor, the extrapolated results agree well with earlier studies, see Section VIII.4.1.4.

The dissociation pressure for the reaction $2ThOI_2(cr) \rightleftharpoons ThO_2(cr) + ThI_4(g)$ was also determined gravimetrically; again an orifice size effect was observed and the appropriate correction made.

The enthalpy of ThI_4(cr, l), contained in nickel, was also measured in a drop calorimeter from 350 to 1030 K. However, very small samples (*ca.* 0.5 g of both ThI_4 and Ni) were used, so it is not surprising that the results, especially for the liquid, are rather scattered. The enthalpy associated with the nickel capsule was not measured independently, but taken from thermochemical tables [1977BAR/KNA]. The molar heat capacity of ThI_4(cr) was calculated to be 146 $J\cdot K^{-1}\cdot mol^{-1}$ and the enthalpy of fusion to be *ca.* 48 $kJ\cdot mol^{-1}$. The results from the measurements of the liquid were too scattered to allow any reliable value of its heat capacity to be derived, but were consistent with the value of 176 $J\cdot K^{-1}\cdot mol^{-1}$ estimated in [1975RAN]. The melting point of ThI_4(cr) was determined to be (839 ± 2) K, from eight different samples.

[1986WAR/KLE]

This is a summary and assessment of the thermodynamic data of elemental thorium, part of a wider review of all the actinide metals. As noted in Section V.1.2, the values from their assessment are very similar to that of [1982GLU/GUR], except for one notable difference.

Ward *et al.* [1986WAR/KLE] quote S°_{m} (Th, cr, 298.15 K) = 52.64 $J\cdot K^{-1}\cdot mol^{-1}$, from [1980NAK/TAK], whereas the value given by [1982GLU/GUR] (and [1989COX/WAG]) is (51.83 ± 0.50) $J\cdot K^{-1}\cdot mol^{-1}$. As noted in Section V.2.1, this review has investigated this discrepancy in detail and recommends another procedure for estimating the poorly defined heat capacities of Th(cr) between 4 and 20 K, which gives precisely the same value of S°_{m} (Th, cr, 298.15 K), 52.64 $J\cdot K^{-1}\cdot mol^{-1}$, as that of [1986WAR/KLE].

[1987BRU/CAS2]

This paper reports potentiometric measurements in the Th(IV)-H_2O-CO_2(g) system at 25°C in 3.0 M $NaClO_4$ under CO_2(g) partial pressures of 0, 0.29 and 0.97 bar. The experimental procedures and conditions were the same as those reported in an extended later study [1991GRE/LAG2], where the data evaluation was discussed more detailed. Therefore the present review does not further consider the preliminary and brief discussion in [1987BRU/CAS2] but only the more detailed discussion and data evaluation in [1991GRE/LAG2].

[1987EDV/LAG]

Four new systems in the molecular spectrum of ThO(g) were rotationally analysed. The molecular constants for the new states are given. However, two of these, the interrelated Y and W states, cannot as yet be placed in the term scheme.

[1987JOA/BIG2]

The equilibrium constants for the formation of complexes between Th^{4+} and $EDTA^{4-}$ and carbonate were determined using a liquid-liquid extraction technique at 20ºC with benzoylacetone and tributylphosphate (TBP) as the extraction ligands. The experiments were made at two different ionic strengths, 1.0 and 2.5 M (guanidinium carbonate ionic media). The complex formation between Th(IV) and EDTA was also determined and used to estimate the equilibrium constants in the Th(IV)-carbonate system as described in detail by Joâo *et al.* [1987JOA/BIG2]. The binary Th(IV)-EDTA system was studied at a total concentration of EDTA = 2.00 mM and pH varying between 10.49 and 10.55, using ammonia and ammonium nitrate to establish the pH and guanidinium nitrate to make up the ionic strength. TBP was used as a synergistic reagent to increase the distribution coefficient of the uncharged $Th(benzoylacetonate)_4$ complex. The carbonate study was made at one carbonate concentration using a test solution containing $[CO_3^{2-}] = [HCO_3^-] = 0.26$ M (at $I = 1.04$ M) and $[CO_3^{2-}] = [HCO_3^-] = 0.50$ M (at $I = 2.50$ M). The pH in these two sets of experiments was constant at 10.18 and 10.22, respectively, at $I = 1.0$ and 2.5 M. The total concentration of Th(IV) in the experiment was 1.12 mM. Under the conditions used, there is no significant dissociation of the benzoylacetone and it seems reasonable to assume that this ligand does not form ternary Th(IV)-carbonate-benzoylacetonate complexes in aqueous solution. The situation is less obvious for the formation of other ternary complexes, such as Th(IV)-EDTA-hydroxide and Th(IV)-carbonate-hydroxide complexes. The equilibrium constant for the reaction

$$\mathrm{Th(EDTA)(aq) + H_2O(l) \rightleftharpoons Th(EDTA)(OH)^- + H^+} \qquad (A.74)$$

at $I = 0.1$ M is known ($\log_{10}K = -7.2$) [1989SMI/MAR]. Recalculation to $I = 1.0$ gives $\log_{10}K = -7.24$, indicating that $Th(EDTA)(OH)^-$ is the predominant complex at the pH of 10.2 used by Joâo *et al.* Their data have therefore been reanalysed. The experimental data on the U(IV)-carbonate system [1989BRU/GRE] indicates that ternary hydroxide-carbonate complexes are not formed in significant amounts under the conditions used in [1987JOA/BIG2]; this is presumably also the case for the corresponding Th(IV) system as discussed in this review.

Joâo *et al.* [1987JOA/BIG2] analysed the experimental distribution data assuming the following reactions in the aqueous phase

$$\mathrm{Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}}; \qquad (A.75)$$

and

$$\mathrm{Th^{4+} + EDTA^{4-} \rightleftharpoons Th(EDTA)(aq)}; \qquad (A.76)$$

The ratio between the experimental distribution coefficients in the carbonate and EDTA systems, D^C and D^Y (with the same notation as in [1987JOA/BIG2]) is

$$\frac{D^C}{D^Y} = \frac{\beta_1^Y[\mathrm{EDTA}]}{\beta_5^C[\mathrm{CO_3^{2-}}]^5} \times \left([\mathrm{H}_Y^+]/[\mathrm{H}_C^+]\right)^4 \qquad (A.77)$$

where β_5^C and β_1^Y are the equilibrium constants for Eqs. (A.75) and (A.76). Joâo *et al.* [1987JOA/BIG2] report $\log_{10} \beta_5^C$ = (26.2 ± 0.2) and (26.3 ± 0.3) at I = 1.0 and 2.5 M, respectively. However, these values are not accepted by the present review, because, as noted earlier, at the pH used the predominant reaction in the EDTA system is

$$\mathrm{Th^{4+} + EDTA^{4-} + H_2O(l) \rightleftharpoons Th(EDTA)(OH)^- + H^+}; \tag{A.78}$$

The equilibrium constant is

$$\frac{[\mathrm{Th(EDTA)(OH)^-}][\mathrm{H^+}]}{[\mathrm{Th^{4+}}][\mathrm{EDTA}]} = K_{111} \tag{A.79}$$

The known equilibrium constants of Eqs. (A.74) and (A.76) [1989SMI/MAR] then give $\log_{10} K_{111}$ = 22.3 − 7.24 = 15.06. Equation (A.77) must then be modified as follows:

$$\frac{D^C}{D^Y} = \frac{K_{111}^Y[\mathrm{EDTA}]/[\mathrm{H}_Y^+]}{\beta_5^C[\mathrm{CO}_3^{2-}]^5} \times \left([\mathrm{H}_Y^+]/[\mathrm{H}_C^+]\right)^4 \tag{A.80}$$

At the given pH of the experiment at ionic strength 1.0 M, the conditional equilibrium constant to be used in Eq. (A.77) is $\log_{10} K_{111}^{\mathrm{cond}} = \log_{10} K_{111}$ + pH = 15.06 + 10.18 = 25.24. Hence, the correct value of $\log_{10} \beta_5$ is 28.3 at I = 1.0 M. This review has accepted the uncertainty of ±0.2 in $\log_{10} \beta_5^C$ proposed in [1987JOA/BIG2]. As the experiments described in [1987JOA/BIG2] were made at constant pH, their slope analysis is not affected by the erroneous composition of the Th(IV) EDTA complex. The recalculated value of $\log_{10} \beta_5^C$ differs significantly from that proposed by Joâo *et al.* [1987JOA/BIG2] at I = 1.0 M, $\log_{10} \beta_5^C$ = (26.2 ± 0.2). Östhols *et al.* [1994OST/BRU] have also recalculated the equilibrium constant for the formation of $\mathrm{Th(CO_3)_5^{6-}}$ using the experimental data in [1987JOA/BIG2] and the equilibrium constant for the formation of $\mathrm{Th(EDTA)(OH)^-}$ from [1989SMI/MAR], valid at I = 0.1 M, and found $\log_{10} \beta_5$ = 33.2 at I = 0.5 M. However, it is not clear how this value was obtained and it has therefore not been considered by the present review. The value $\log_{10} \beta_5$ = 28.3 at I = 1.0 M, obtained as described above, is much lower than the selected value of (31.0 ± 0.7) which consistently describes both the EXAFS data in [1997FEL/RAI] and [2006ALT/NEC] and the solubility data involving $\mathrm{Na_6Th(CO_3)_5{\cdot}12H_2O(s)}$ [1961LUZ/KOV2], [1973DER/FAU3] and $\mathrm{ThO_2}$(am, hyd) [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC], [2006ALT/NEC]. With the value of $\log_{10} \beta_5$ = 28.3 from Joâo *et al.* [1987JOA/BIG2] the pentacarbonate complex would not become predominant – see Figures XI-7 and XI-8 in Section XI.1.3.3.

Since the interaction coefficients between $\mathrm{Th^{4+}}$ and $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$ and those between the guanidinium cation and the anions $\mathrm{CO_3^{2-}}$ and $\mathrm{Th(CO_3)_5^{6-}}$ are not known, the recalculated value of $\log_{10} \beta_5$ = 28.3 in guanidinium carbonate solution (I = 1.0 M) cannot be extrapolated to zero ionic strength, but as the Δz^2 term in the SIT equation is equal to zero we may assume that the corresponding $\log_{10}\beta_5^\circ$ value differs by less than ± 1.0 from the value at I = 1.0 M.

[1987OET/PET]

Well characterised thorium metal, whose principal impurities were 0.16 at% C, 0.02 at% O and 0.015 at% N, was used in 83 measurements of the enthalpy difference $H_\mathrm{m}(T) - H_\mathrm{m}^\circ(298.15\,\mathrm{K})$ from 302.6 to 694.9 K, with a reproducibility of *ca.* 1% (2σ). The values were adjudged by the authors to be accurate to within 0.2%, based on similar measurements on a sample NBS/NIST standard reference molybdenum. The results were close to the laser flash measurements of [1980NAK/TAK] and thus to the values selected in this review.

[1987RYA/RAI]

Ryan and Rai [1987RYA/RAI] note that there is contradictory information in the literature on the possible formation of anionic complexes $\mathrm{Th(OH)_5^-}$; their own solubility studies on other actinides, reviewed in [2003GUI/FAN] very clearly indicate that the hydrous oxides of tetravalent actinides are not amphoteric. To settle the matter they have performed a solubility study of hydrous thorium oxide over a broad pH range, where the hydroxide concentration extends to 1.38 M. The experiments have been made at 25°C in a 0.1 M $\mathrm{NaClO_4}$ ionic medium, except at pH > 11 where the hydroxide concentration and accordingly the ionic strength, varies by the use of tetraethylammonium hydroxide or lithium hydroxide. The experiments are described in detail and care has been taken to separate the solid phase, part of which is in colloidal form, from the solution. The thorium concentration was measured by neutron activation analysis after centrifugation and ultrafiltration of samples equilibrated for 7 − 27 days. There is no indication of a variation in solubility from pH 6 up to the highest hydroxide concentration. However, the measured solubility $10^{-9} - 10^{-10}$ M is close to the detection limit of the analytical method used. These data support the assumption that anionic hydroxide complexes are not formed in this system.

The authors note that the slope − 5.5 of the initial part of the solubility curve indicates the formation of polynuclear complexes with charge Z > 4, because the species $\mathrm{Th(OH)^{3+}}$ and $\mathrm{Th(OH)_2^{2+}}$ would result in a slope of − 3 to − 2. By using the equilibrium constants proposed by Baes and Mesmer [1976BAE/MES] for $\mathrm{Th(OH)^{3+}}$ and $\mathrm{Th(OH)_2^{2+}}$ and estimating the activity coefficients for the reactants, Ryan and Rai suggest $\log_{10} K_{s,0}^\circ = -45.9$ for the reaction:

$$\mathrm{ThO_2(am) + 2H_2O(l) \rightleftharpoons Th^{4+} + 4OH^-}$$

Ryan and Rai emphasise that there is a large difference between the experimental solubility product of $\mathrm{ThO_2(am)}$ and the considerably lower value of $\log_{10} K_{s,0}^\circ$ ($\mathrm{ThO_2}$, cr) = − 54.14 which they calculated for crystalline $\mathrm{ThO_2(cr)}$ from thermochemical data. The latter value is close to $\log_{10} K_{s,0}^\circ$ ($\mathrm{ThO_2}$, cr) = − (54.24 ± 1.11) calculated in the present review but significantly different from the one proposed by Baes and Mesmer [1976BAE/MES], $\log_{10} K^{\circ}_{s,0}$ (ThO_2, cr) = −49.4.

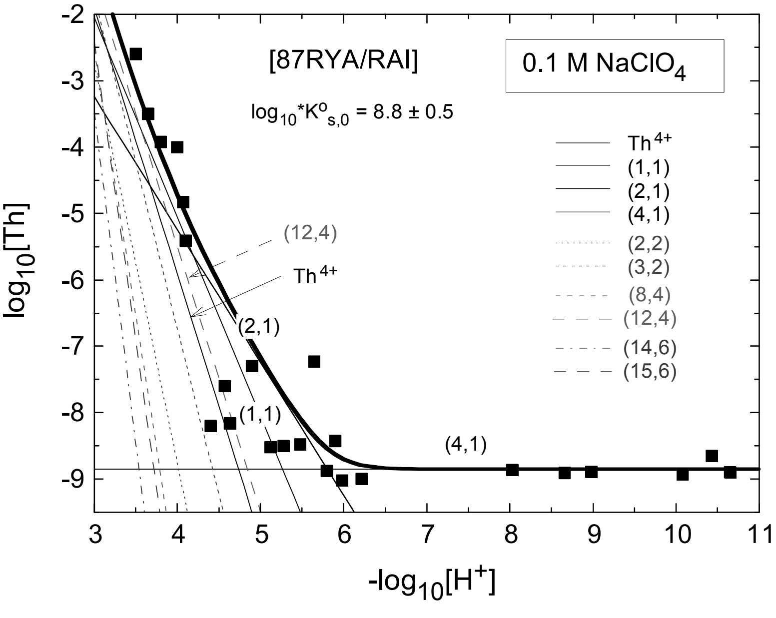
Based on the solubility product $\log_{10} K^{\circ}_{s,0}$ (ThO_2(am, hyd)) = −(45.9 ± 0.5) ($\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO_2(am, hyd)) = (10.1 ± 0.5)) and the experimental data in neutral and alkaline solutions, Ryan and Rai calculated upper limits of $\log_{10} {}^{*}\beta_4 \leq -19.7$, $\log_{10} {}^{*}\beta_5 \leq -33.1$, and $\log_{10} K_{s,5} < -9$ for the reaction:

$$ThO_2(am) + 2H_2O(l) + OH^- \rightleftharpoons Th(OH)_5^- .$$

Accordingly, the maximum concentration of $Th(OH)_5^-$ is below 10^{-9} M at $[OH^-]$ = 1.0 M which shows that, contrary to results reported in the previous literature, anionic hydroxide complexes are negligible under ordinary chemical conditions.

Using the hydrolysis constants and SIT coefficients selected in the present review, the re-evaluation of Ryan and Rai's solubility data at pH < 6 yields $\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO_2(am, hyd)) = (8.8 ± 0.5) ($\log_{10} K^{\circ}_{s,0} = -(47.2 \pm 0.5)$). As shown in Figure A-31, the species $Th_4(OH)_{12}^{4+}$, $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$ are predominant in saturated solutions at pH < 5.5. The mean value of the experimental solubility data at pH > 6 in 0.1 M $NaClO_4$ gives $\log_{10} K^{\circ}_{s,4} = -(8.8 \pm 0.4)$ and $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.6 \pm 0.6)$.

Figure A-31: Solubility data for ThO_2(am, hyd) in 0.1 M $NaClO_4$ [1987RYA/RAI]: Recalculation of the solubility constant and aqueous speciation using the hydrolysis constants and SIT coefficients selected in the present review.



[1988EDV/LAG]

Two new systems in the molecular spectrum of ThO(g) were rotationally analysed and the molecular constants for two new excited states designated A' and B' are given.

[1989GRA/KIN]

The enthalpy of reaction for the formation of ThF_n^{4-n}, $n = 1-3$, have been determined calorimetrically at 25°C in a 0.5 M $NaClO_4$ ionic medium. The experiments were made by titrating a test solution of 20 mM Th^{4+} with an initial pH (presumably $-\log_{10}[H^+]$) of 1.1 with a solution of 0.1000 M NaF. In addition the authors made a separate experiment to determine the enthalpy of protonation of F^- and the enthalpy of dilution of the NaF titrant. The experiments were carried out until precipitation occurred at $\overline{n_F} \approx 1.7$. The equilibrium constants used to interpret the titration data were taken from [1982MAR/SMI]. The authors have use state of the art equipment and methodology and taken care to minimise systematic errors. This is very important in view of the small reaction enthalpies, corresponding to about 40 mJ for the individual additions of the titrant. This is a very precise experimental study and the conclusions drawn by the authors are accepted by this review.

Table A-61 gives a list of the thermodynamic quantities quoted by [1989GRA/KIN]. The authors have also determined the enthalpy of protonation of F^- using their calorimetric method. This provides an independent method to compare the accuracy of the system using a reaction with a larger enthalpy change. They found an enthalpy of protonation of (12.38 ± 0.38) kJ·mol^{-1}, as compared to literature values 12.2 kJ·mol^{-1} [1967AHR] and 13.0 kJ·mol^{-1} [1969AZI/LYL] and the standard value of 12.15 kJ·mol^{-1} (calculated from Table IV-1).

Table A-61: Thermodynamic quantities for the reactions $Th^{4+} + nF^- \rightleftharpoons \mathrm{ThF}_n^{4-n}$ at 25°C and $I_c = 0.5$ M ($NaClO_4$).

Complex	n	$-\Delta_r G_m$ (kJ·mol^{-1})	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})
ThF^{3+}	1	43.3 ± 0.24	1.6 ± 0.03	150 ± 0.8
ThF_2^{2+}	2	76.7 ± 0.12	4.3 ± 0.07	272* ± 0.5
ThF_3^+	3	102 ± 0.64	7.8 ± 0.9	370 ± 4

* reported as 270 in [1989GRA/KIN]

The Gibbs energy values and uncertainties in Table A-61 are from [1982MAR/SMI]. The uncertainties in $\Delta_r H_m$ are given at the 1σ level and those in $\Delta_r S_m$ are obtained by combining the uncertainties in the previous quantities.

The reported enthalpies of reaction are positive, in contrast to the values reported by [1990AHR/HEF] in 4.0 M $HClO_4$, $\Delta_r H_1 = -(2.4 \pm 0.1)$ and $\Delta_r H_2 = -(3.3 \pm 0.4)$ kJ·mol^{-1} and by Choppin and Unrein [1976CHO/UNR] in 1.0 M $HClO_4$,

$\Delta_r H_n$ equal to -1.1, -2.2 and -3.0 kJ·mol^{-1} for $n = 1-3$, respectively. The uncertainties in the experimental values are given as one standard deviation from the least-squares method used. The enthalpies of reaction for the formation of the thorium fluoride complexes are small and the numerical values are thus very sensitive to systematic errors such as those resulting from the different ionic media used. A comparison of the calorimetric investigations indicates that the reported experimental uncertainties have not been taken this into account. For the reasons discussed in Section VIII.1.2.2 this review has only selected values for $\Delta_r H_1^o$ and $\Delta_r H_2^o$, but not for $\Delta_r H_3^o$. The selected values are:

$$\Delta_r H_1^o = -(0.4 \pm 2.0)\ \text{kJ·mol}^{-1}$$

$$\Delta_r H_2^o = -(3.3 \pm 0.4)\ \text{kJ·mol}^{-1}.$$

[1989LAU/BRI]

The gaseous species ThF, ThF_2, ThF_3, and ThF_4 were generated in a heated effusion beam source, and were identified and characterised by mass spectrometry, together with the gaseous oxyfluoride ThOF, arising from an oxygen impurity in the sample. Equilibria involving the reactions of these species with Ba(g) and BaF(g) were studied over considerable temperature ranges. The vapour pressure of ThF_4(cr) was also determined. The thermochemical properties of the Th-F species are derived and the data are compared to those of the corresponding uranium fluorides.

Data are also given for the reaction $ThO(g) + BaF(g) \rightleftharpoons ThOF(g) + Ba(g)$, leading to the enthalpy of formation of ThOF(g).

The sample of ThF_4(cr) used was stated to be 99.9% pure by the suppliers, and was not analysed further. The vapour pressure of the solid was determined by torsion effusion from two graphite cells with diameters differing by a factor of eight, from 1047 to 1201 K. No orifice-size effect was found.

All these data are analysed in Sections VIII.1.1.1.2, VIII.1.1.3.2 and VIII.1.1.4.

[1989LAU/HIL]

The decomposition pressure of $ThOF_2$(cr) was measured by torsion-effusion from 1088 to 1248 K. The solid oxyfluoride vaporises incongruently to give ThF_4(g) and ThO_2(cr). The composition of the vapour was confirmed by mass spectrometry. A small effusion orifice-area dependence indicates, not unexpectedly, a slight kinetic barrier to the incongruent vaporisation process. Although the results with the two cells overlapped only over the range 1133 to 1191 K, the temperature coefficients were very similar and the vapour pressures were therefore extrapolated up or down to cover the range 1100 to 1200 K, and fitted values extrapolated to zero orifice size.

The decomposition pressures were only about a factor of two smaller than the vapour pressure of pure ThF_4(cr) measured by the same authors [1989LAU/BRI], and agree excellently with those of Darnell [1960DAR]. The results were processed by the second-law to give the enthalpy of formation and standard entropy of the solid oxyfluoride. The oxyfluoride is only marginally stable with respect to ThO_2(cr) and ThF_4(cr).

[1989MOO]

Moon has used a combination of solubility experiments and 1 nm-ultrafiltration to determine hydrolysis constants of Th(IV) in 0.1 M and 0.5 M $NaClO_4$ media at 18°C. The solubility of crystalline ThO_2(cr) has been measured at pH 1.5 − 13 in 0.1 M $NaClO_4$ and the solubility of amorphous $Th(OH)_4$(am) at pH 4 − 13 in 0.5 M $NaClO_4$. The ultrafiltration is used to remove particles from the equilibrium solutions, after which the total concentration of Th was determined by neutron activation analysis. The pH values were determined with a Orion Ross electrode and converted into $\log_{10}[OH^-]$. No details are reported in this paper, but the procedures used at that time in this laboratory are described in other papers, *e.g.*, in [1986LIE/KIM] where Moon's results were cited and compared to data for Pu(IV). The resulting solubility curves were analysed using a least-squares method with known equilibrium constants as starting values; the deduced equilibrium constants are shown in Table A-62.

Table A-62: Equilibrium constants for the reactions $m\mathrm{Th}^{4+} + n\mathrm{OH}^- \rightleftharpoons \mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$ in 0.1 M and 0.5 M $NaClO_4$ at 18°C.

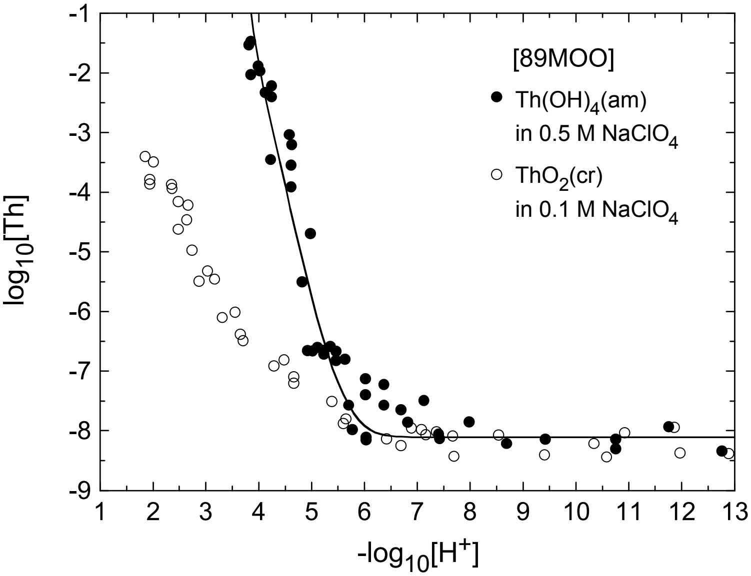
Complex	$\log_{10}\beta_{n,m}$ (0.1 M $NaClO_4$)	$\log_{10}\beta_{n,m}$ (0.5 M $NaClO_4$)
$Th(OH)^{3+}$	12.42 ± 0.02	12.58 ± 0.02
$Th(OH)_2^{2+}$	22.46 ± 0.15	22.33 ± 0.15
$Th(OH)_3^{+}$	34.36 ± 0.07	34.42 ± 0.07
$Th(OH)_4$	42.58 ± 0.08	42.76 ± 0.08
$Th_2(OH)_2^{6+}$	22.11 ± 0.10	30.05 ± 0.04
$Th_2(OH)_3^{5+}$	–	32.21 ± 0.11
$Th_2(OH)_4^{4+}$	–	59.07 ± 0.04
Solid phase	$\log_{10}K_{s,0}$ (0.1 M $NaClO_4$)	$\log_{10}K_{s,0}$ (0.1 M $NaClO_4$)
ThO_2(cr)	– 50.76 ± 0.08	
$Th(OH)_4$(am)		– 50.52 ± 0.08

The experimental data of [1989MOO] are comparable with the results of similar studies [1964NAB/KUD], [1991FEL/RAI], [2000RAI/MOO]; however, the data evaluation shows many shortcomings. To begin with, in the solubility study with $Th(OH)_4$(am) there is no significant concentration of Th^{4+} in the test solutions with the lowest value of pH. Hence it is not possible to determine the solubility product from these data; the reported value is nearly the same as for $ThO_2(cr)$. In addition the concentration of $Th(OH)^{3+}$ is very small, reaching at most a few percent of the total concentration of thorium. It is not possible to determine a precise value of the equilibrium constant under these conditions; the experimental data will most likely be well described also with a model where $Th(OH)^{3+}$ is not included. Nevertheless, the author reports equilibrium constants with surprisingly small uncertainties. Another example of data inconsistency is the large difference in the equilibrium constant for $Th_2(OH)_2^{6+}$ between 0.1 and 0.5 M $NaClO_4$; eight orders of magnitude is not consistent with the expected variation due to activity factor changes. The difference is understandable if the complex is a computational artefact. The author has made the mistake of not comparing different chemical models to see if a unique one can be established, or not. An analysis of this type also gives a much better estimate of the uncertainty in the equilibrium constants. The shortcomings of this study are so large that the equilibrium constants proposed cannot be considered in the final selection of data.

Moon's experimental data for $Th(OH)_4(am)$ in 0.5 M $NaClO_4$, typical for solubility studies of this type, have been re-evaluated using the hydrolysis constants and SIT coefficients selected in the present review. From the data at pH < 6 a solubility constant of $\log_{10}{}^*K^\circ_{s,0} = (9.5 \pm 0.3)$ ($\log_{10} K^\circ_{s,0} = -(46.5 \pm 0.3)$) is obtained. The mean value of the experimental solubility data at pH > 6 in 0.1 M $NaClO_4$ gives $\log_{10} K^\circ_{s,4} = -(8.1 \pm 0.3)$ and $\log_{10}{}^*\beta^\circ_{4,1} = -(17.6 \pm 0.4)$.

At low pH values Moon's solubility data for $ThO_2(cr)$ are significantly lower than the values for $Th(OH)_4(am)$, but with increasing pH, the solubility of the crystalline oxide continuously approaches the thorium concentration in equilibrium with amorphous thorium hydroxide. At pH > 5 the data measured with $ThO_2(cr)$ and $Th(OH)_4(am)$ are the same (Figure A-32). An interpretation of this unexpected behaviour is presented in Section VII.4.3. Only the data at the lowest pH values actually refer to crystalline $ThO_2(cr)$. With increasing pH, the total solubility is given by smaller particles present in the solid. At pH > 5, the solubility is determined by a small fraction of "$Th(OH)_4(am)$" particles < 5 nm.

Figure A-32: Comparison of solubility data measured by Moon [1989MOO] with $Th(OH)_4(am)$ in 0.5 M $NaClO_4$ and with $ThO_2(cr)$ in 0.1 M $NaClO_4$ at 18°C. The solubility curve for ThO_2(am, hyd) is calculated using the hydrolysis constants and SIT coefficients selected in the present review, in combination with $\log_{10}{}^*K^{\circ}_{s,0} = 9.5$ and $\log_{10} K^{\circ}_{s,4} = -(8.1 \pm 0.3)$.



[1990AHR/HEF]

Ahrland *et al.* report calorimetric studies of mononuclear fluoride complexes of Zr(IV), Hf(IV), U(IV) and Th(IV). Only the experimental data for Th(IV) will be discussed here. The enthalpy of reaction for the formation of ThF^{3+} and ThF_2^{2+} have been determined using calorimetry together with previous information on the equilibrium systems [1969NOR] for the Th(IV) data. This is a precise experimental study and the thermodynamic data are accordingly more precise than those in [1976CHO/UNR]. The experiments are described in detail together with the primary experimental data and these results are accepted by the present review. The reaction values at 298.15 K were: $Th^{4+} + F^- \rightleftharpoons ThF^{3+}$: $\Delta_r G^{\circ}_m(ThF^{3+}) = -46.6$ kJ·mol^{-1}, $\Delta_r H^{\circ}_m(ThF^{3+}) = -(2.4 \pm 0.1)$ kJ·mol^{-1}, $Th^{4+} + 2F^- \rightleftharpoons ThF_2^{2+}$: $\Delta_r G^{\circ}_m(ThF_2^{2+}) = -83.1$ kJ·mol^{-1}, $\Delta_r H^{\circ}_m(ThF_2^{2+}) = -(3.3 \pm 0.4)$ kJ·mol^{-1}.

The thermodynamic quantities used by [1990AHR/HEF] for the protonation of F^-:

$$H^+ + F^- \rightleftharpoons HF(aq) \qquad (A.81)$$

are $-\Delta_r G^\circ_m$ (A.81) = 20.2 kJ·mol^{-1}, $\Delta_r H^\circ_m$ (A.81) = 11.9 kJ·mol^{-1} and $\Delta_r S^\circ_m$ (A.81) = 108 J·K^{-1}·mol^{-1}.

[1990BAZ/EZH]

The authors have studied the structure and vibrational features of $ThCl_4(g)$ using gas electron diffraction. The sample of $ThCl_4(cr)$ contained less than 0.5% impurities (mainly $ThO_2(cr)$), and was vaporised from a molybdenum capsule, which spectroscopic investigations have shown gives essentially only monomeric species.

The results strongly suggested that $ThCl_4(g)$ has tetrahedral T_d symmetry, with a Th–Cl bond distance of 2.567 Å, although a slight distortion of the tetrahedral structure could not be entirely excluded. Assuming the T_d structure, a simple force field analysis with two force constants gave vibration frequencies of (330 ± 30), (80 ± 15), (370 ± 30), and (75 ± 15) cm^{-1}. These are in quite good agreement with those obtained from more recent density functional calculations. The internuclear distance inferred by [1990BAZ/EZH] has been used in the calculations of the thermal functions of $ThCl_4(g)$.

[1990ELY/BRI]

The authors have explored the equilibria in the Th(IV)-H_3PO_4-$LiClO_4$ system using liquid-liquid extraction (with HDEHP in benzene as the extracting ligand). The experiments have been made at a constant ionic strength of 0.2 M at 25°C. There is no information about the temperature; this review assumes that the data refer to 20−25°C. The paper provides details about the experimental methods and the data analysis and the experimental observations can be well described by the proposed chemical model. This consists of the following species:

$$\log_{10} K\,(\mathrm{Th(OH)(H_2PO_4)^{2+}}) = (5.22 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(OH)_2(H_2PO_4)^{+}}) = (3.62 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(H_2PO_4)^{2+}}) = (5.65 \pm 0.05)$$

$$\log_{10} K\,(\mathrm{Th(OH)(H_2PO_4)_2^{+}}) = (4.70 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(OH)(H_2PO_4)_3, aq}) = (2.90 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(H_2PO_4)_4, aq}) = (3.86 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(OH)_2(H_2PO_4)_5^{3-}}\ \text{or}\ \mathrm{Th(H_2PO_3)_3(HPO_4)_2^{3-}}) = -(3.65 \pm 0.13)$$

The stoichiometry of the complexes, which cannot be determined from the equilibrium data because of the proton ambiguity ($\mathrm{Th(OH)(H_2PO_4)_2^{+}} \equiv \mathrm{Th(HPO_4)(H_2PO_4)^{+}}$), has instead been estimated based on partial atomic charges. Despite the care taken both in the experiments and the data analysis, the present review does not accept the stoichiometry and the equilibrium constants proposed; the reasons are: there is a large number of parameters in the model used and only one single model has been tested. In particular one would have liked to see if a model with some of the minor complexes removed could describe the data within the estimated experimental uncertainty. In addition, the reviewers are not confident that the electrostatic considerations are justified to deduce the stoichiometry of the complexes; in particular we notice that hydroxide coordination is assumed to occur even in the pH range where hydrolysis in the binary Th(IV)-hydroxide system is small or negligible; this is in the opinion of the reviewers not likely.

[1990HIL/LAU]

The sublimation of $ThBr_4$(cr) was studied in the temperature range 631 to 768 K by the torsion-effusion method. Supplementary mass-spectrometric measurements indicated that only monomeric $ThBr_4$(g) exists in the vapour at these temperatures, in agreement with the molecular weight derived from the torsion-effusion measurements. The entropy of sublimation was considered to be more consistent with a distorted tetrahedral structure, but later theoretical studies indicate that the $ThBr_4$(g) molecule, in fact has tetrahedral symmetry, as discussed in Section VIII.3.1.4.1.

The gaseous lower-valent species $ThBr_3$, $ThBr_2$, and ThBr were identified in the bromination of Th(cr) at 1500 to 2000 K, and the equilibria involving Th(g), ThBr(g), $ThBr_2$(g) and Br(g) were studied by mass-spectrometry from 1986 to 2455 K. Addition of aluminium to the system allowed the equilibria involving Al(g), AlBr(g), $ThBr_2$(g), $ThBr_3$(g) and $ThBr_4$(g) to be studied from 1696 to 1935 K. Reaction enthalpies, bond dissociation energies, and enthalpies of formation were derived from the results by second law analyses. However, the precise values of the thermal functions used by the authors for correction to 298.15 K are not entirely clear, especially for ThBr(g).

All these data are analysed in detail in Section VIII.3.1.1.

[1990LAU/HIL]

The sublimation of $ThCl_4$(cr) was studied in the temperature range 685 to 775 K by the torsion-effusion method. Supplementary mass-spectrometric measurements indicated that only monomeric $ThCl_4$(g) exists in the vapour at these temperatures, in agreement with the molecular weight derived from the torsion-effusion measurements. The entropy of sublimation was considered to be consistent with a tetrahedral structure, as confirmed by later theoretical studies, as discussed in Section VIII.2.1.4.1

The gaseous lower-valent species $ThCl_3$, $ThCl_2$, and ThCl were identified in the chlorination of Th(cr) with either Cl_2(g) or $CaCl_2$(g) , and the equilibria involving Th(g), ThCl(g), $ThCl_2$(g), $ThCl_3$(g) and Ca(g) and CaCl(g) were studied by mass-spectrometry in various temperature ranges from 2003 to 2478 K. Reaction enthalpies, bond dissociation energies, and enthalpies of formation were derived from the results by second law analyses. However, the precise values of the thermal functions used by the authors for correction to 298.15 K are not entirely clear, especially for ThCl(g).

All these data are analysed in Section VIII.2.1.2.

[1990SAW/CHA2]

There is an extensive review of this paper in [2001LEM/FUG] and we will only make a short summary of the paper and some additional comments. The experimental data were obtained using potentiometric titrations of Th(IV) with HF using a fluoride selective electrode. The ionic medium was 1 M $(Na,H)ClO_4$ and the measurements were made at (23 ± 2)°C and using a least-squares program (MINIQUAD) for the determination of equilibrium constants and their estimated uncertainty. Primary experimental data for the Th(IV) system are given in Table 3 of [1990SAW/CHA2]; the total concentrations of Th_{tot}, H_{tot} and F_{tot} varied from 20.66 to 10.88 mM, 483.3 to 254.8 mM and 2.11 to 48.4 mM, respectively. The high hydrogen ion concentration results in negligible hydrolysis of Th(IV). The experimental data up to $\bar{n}_F$ around 1.8 seems to be satisfactory, but then the curve increases steeply as previously found in [1949DOD/ROL] and [1971KLO/MUK]; indicating the precipitation of $ThF_4(s)$. However, Sawant *et al.* make no comment about this and describe the experimental data using a set of four complexes, ThF_n^{4-n} and corresponding equilibrium constants. The model is correct but the reported values of equilibrium constants, especially for $ThF_4(aq)$, are questionable and are not accepted by this review. The $\log_{10} \beta_n$ values obtained by the least-squares analysis are reported in [1990SAW/CHA2] as: $\log_{10} \beta_1 = (7.61 \pm 0.01)$; $\log_{10} \beta_2 = (13.42 \pm 0.05)$; $\log_{10} \beta_3 = (17.65 \pm 0.2)$ and $\log_{10} \beta_4 = (23.67 \pm 0.11)$, where this review has estimated the uncertainty of the two first constants to be twice as large as suggested in [1990SAW/CHA2]. Based on the appropriate ion-interaction parameters reported in Table VIII-8 for this system, this review calculated values of $\log_{10} \beta_1^{\circ} = (9.00 \pm 0.14)$; $\log_{10} \beta_2^{\circ} = (15.84 \pm 0.16)$; $\log_{10} \beta_3^{\circ} = (20.66 \pm 0.26)$, which are fairly similar to the values recommended in this review. Since [1990SAW/CHA2] report their raw data, it is of interest to determine how closely the aqueous phase model recommended in this review reproduces the experimental data. For this purpose, the observed fluoride activities reported by [1990SAW/CHA2] are compared with the fluoride activities calculated from the aqueous phase model that included values for β_1° through β_4° (Figure A-33). These comparisons indicate very close agreement between the experimental and the predicted concentrations at low fluoride activities, approximately at $\log_{10}[F^-] < -5.6$. The disagreement at higher fluoride activities, about $\log_{10}[F^-] > -5.6$, is expected as a result of possible complications due to the precipitation of ThF_4(cr, hyd). The distribution of different species is listed in Table A-63.

Figure A-33: Observed ([1990SAW/CHA2]) and predicted F^- activities at (23 ± 2)°C for potentiometric titrations using fluoride-selective electrode in 1 M $(H,Na)ClO_4$ solutions. Predictions based on NONLINT-SIT calculations using the thermodynamic model summarised in Tables VIII-8 and VIII-9.

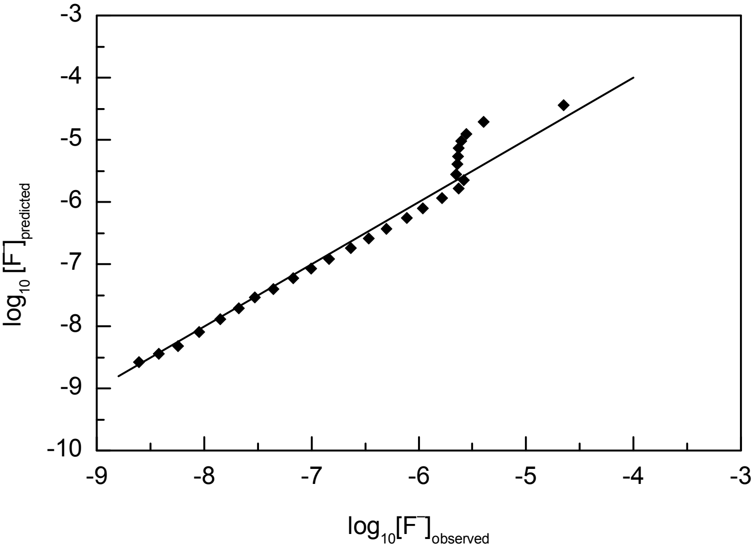


Table A-63: Experimental ([1990SAW/CHA2]) and predicted concentrations of different species at (23 ± 2)°C for potentiometric titrations using fluoride-selective electrode in 1 M (H, Na)ClO_4 solutions. Predictions based on NONLINT-SIT calculations using the thermodynamic model summarised in Tables VIII-8 and VIII-9.

Experimental concentrations (m)						Predicted concentrations (m)[a]						
H_{Total}	Na_{total}	$(ClO_4)_{total}$	Th_{Total}	F_{Total}	$F^-_{activity}$	$F^-_{activity}$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	$ThF_4(aq)$	ThF_6^{2-}
4.833E-01	4.341E-01	9.979E-01	2.066E-02	2.106E-03	2.491E-09	2.630E-09	1.856E-02	2.096E-03	4.365E-06	4.732E-10	7.944E-14	7.000E-14
4.801E-01	4.378E-01	9.973E-01	2.052E-02	2.748E-03	3.792E-09	3.565E-09	1.778E-02	2.730E-03	7.730E-06	1.138E-09	2.594E-13	7.000E-14
4.762E-01	4.424E-01	9.965E-01	2.035E-02	3.544E-03	5.690E-09	4.842E-09	1.682E-02	3.514E-03	1.353E-05	2.706E-09	8.374E-13	7.000E-14
4.679E-01	4.521E-01	9.948E-01	2.000E-02	5.231E-03	9.025E-09	8.054E-09	1.481E-02	5.160E-03	3.309E-05	1.101E-08	5.663E-12	7.000E-14
4.583E-01	4.634E-01	9.928E-01	1.959E-02	7.172E-03	1.412E-08	1.291E-08	1.250E-02	7.019E-03	7.244E-05	3.872E-08	3.194E-11	7.000E-14
4.491E-01	4.741E-01	9.910E-01	1.920E-02	9.023E-03	2.107E-08	1.936E-08	1.032E-02	8.740E-03	1.358E-04	1.090E-07	1.350E-10	7.000E-14
4.414E-01	4.831E-01	9.890E-01	1.887E-02	1.095E-02	2.974E-08	2.904E-08	8.182E-03	1.044E-02	2.443E-04	2.948E-07	5.479E-10	7.000E-14
4.330E-01	4.930E-01	9.877E-01	1.851E-02	1.229E-02	4.384E-08	3.954E-08	6.611E-03	1.153E-02	3.680E-04	6.052E-07	1.531E-09	7.000E-14
4.248E-01	5.026E-01	9.860E-01	1.816E-02	1.396E-02	6.715E-08	5.916E-08	4.845E-03	1.270E-02	6.089E-04	1.502E-06	5.691E-09	7.000E-14
4.182E-01	5.103E-01	9.847E-01	1.787E-02	1.529E-02	9.915E-08	8.472E-08	3.554E-03	1.339E-02	9.212E-04	3.257E-06	1.768E-08	7.000E-14
4.124E-01	5.171E-01	9.835E-01	1.763E-02	1.647E-02	1.457E-07	1.197E-07	2.572E-03	1.372E-02	1.334E-03	6.664E-06	5.105E-08	7.000E-14
4.058E-01	5.248E-01	9.822E-01	1.735E-02	1.780E-02	2.306E-07	1.807E-07	1.686E-03	1.364E-02	2.010E-03	1.519E-05	1.760E-07	7.000E-14
4.002E-01	5.314E-01	9.811E-01	1.710E-02	1.895E-02	3.415E-07	2.594E-07	1.131E-03	1.315E-02	2.784E-03	3.020E-05	5.016E-07	7.000E-14
3.942E-01	5.384E-01	9.799E-01	1.685E-02	2.014E-02	5.010E-07	3.690E-07	7.421E-04	1.233E-02	3.724E-03	5.757E-05	1.363E-06	7.000E-14
3.869E-01	5.470E-01	9.784E-01	1.654E-02	2.164E-02	7.713E-07	5.572E-07	4.367E-04	1.097E-02	5.010E-03	1.169E-04	4.176E-06	7.000E-14
3.802E-01	5.548E-01	9.770E-01	1.625E-02	2.299E-02	1.098E-06	7.852E-07	2.697E-04	9.583E-03	6.183E-03	2.037E-04	1.026E-05	2.667E-13
3.720E-01	5.644E-01	9.753E-01	1.590E-02	2.465E-02	1.654E-06	1.164E-06	1.483E-04	7.839E-03	7.518E-03	3.677E-04	2.747E-05	1.577E-12
3.646E-01	5.731E-01	9.738E-01	1.558E-02	2.616E-02	2.368E-06	1.637E-06	8.475E-05	6.316E-03	8.531E-03	5.870E-04	6.165E-05	7.021E-12
3.576E-01	5.813E-01	9.724E-01	1.528E-02	2.756E-02	2.645E-06	2.218E-06	4.976E-05	5.032E-03	9.217E-03	8.591E-04	1.222E-04	2.559E-11
3.520E-01	5.879E-01	9.713E-01	1.504E-02	2.871E-02	2.224E-06	2.805E-06	3.213E-05	4.119E-03	9.558E-03	1.128E-03	2.029E-04	6.828E-11
3.421E-01	5.994E-01	9.693E-01	1.462E-02	3.070E-02	2.283E-06	4.083E-06	1.522E-05	2.851E-03	9.657E-03	1.661E-03	4.356E-04	3.128E-10
3.337E-01	6.092E-01	9.676E-01	1.426E-02	3.241E-02	2.312E-06	5.433E-06	8.252E-06	2.062E-03	9.311E-03	2.134E-03	7.448E-04	9.529E-10
3.235E-01	6.212E-01	9.655E-01	1.383E-02	3.448E-02	2.348E-06	7.362E-06	4.110E-06	1.394E-03	8.532E-03	2.648E-03	1.252E-03	2.954E-09
3.137E-01	6.327E-01	9.635E-01	1.341E-02	3.646E-02	2.504E-06	9.528E-06	2.167E-06	9.527E-04	7.559E-03	3.038E-03	1.858E-03	7.395E-09
3.032E-01	6.450E-01	9.614E-01	1.296E-02	3.859E-02	2.780E-06	1.227E-05	1.105E-06	6.266E-04	6.407E-03	3.315E-03	2.610E-03	1.733E-08
2.823E-01	6.695E-01	9.572E-01	1.206E-02	4.283E-02	4.013E-06	1.954E-05	2.784E-07	2.525E-04	4.126E-03	3.406E-03	4.275E-03	7.320E-08
2.696E-01	7.378E-01	1.001E+00	1.145E-02	5.088E-02	2.234E-05	3.589E-05	3.610E-08	6.021E-05	1.807E-03	2.734E-03	6.289E-03	3.688E-07

a: All 7.000E-14 numbers are model limiting values, the actual value is lower than this.

[1991FEL/RAI]

This paper is discussed together with [1997RAI/FEL].

These two papers include experimental solubility studies with Th(IV) hydrous oxide in various chloride ionic media: 0.6 M NaCl and KCl, 1.2 and 3.0 M NaCl [1991FEL/RAI], 4.0 and 6.0 m NaCl, 1.82, 1.0 and 3.0 m $MgCl_2$ [1997RAI/FEL]. The solubility experiments were performed at room temperature (*ca.* 22ºC) from undersaturation with amorphous ThO_2(am, hyd) precipitates, purified by washing with water. All experimental details are provided. The results were assumed by this review to be valid for 298.15 K. The operational pH values measured in these chloride solutions with a combined glass-electrode (ROSS type) were converted into H^+ concentrations ($pc_{H^+} = -\log_{10}[H^+]$) using appropriate calibration procedures. The important separation of the test solutions from colloidal hydrous oxide was achieved by centrifugation and using filters with a cutoff limit of 2.5 kDa. The lowest solubilities were measured with ICP-MS ensuring an analytical uncertainty of at most 10%. The measurements were made in the range $3 < -\log_{10}[H^+] < 10.5$ with short (5 − 8 days) and long (51 − 372 days) equilibration times. The experimental data are given as plots of $\log_{10}$ [Th] *vs.* $-\log_{10}[H^+]$ and in an Appendix of [1991FEL/RAI]; they scatter significantly as invariably found in studies of this type. The solubility is approximately constant at $-\log_{10}[H^+] > 6$, indicating that an uncharged complex is predominating here [1991FEL/RAI].

Felmy *et al.* [1991FEL/RAI] interpreted the solubility data at $-\log_{10}[H^+] < 6$ in 0.6 − 3.2 m NaCl and in 0.10 M $NaClO_4$ using the ion interaction approach of Pitzer. The observed solubility in 0.1 M $NaClO_4$ from [1987RYA/RAI] was three to four orders of magnitude lower than in 0.6 M NaCl [1991FEL/RAI]. The specific ion interactions between Th^{4+} and Cl^- and between Th^{4+} and ClO_4^- are very different and must influence the activity coefficient of Th^{4+} significantly. Binary Pitzer parameters for the interaction Th^{4+}-Cl^- and the standard Gibbs energy of formation of Th^{4+} were taken from [1973PIT/MAY] and [1976FUG/OET], respectively. This model was refined in [1997RAI/FEL] including the solubility studies in up to 6.0 m NaCl and 1.0 − 3.0 m $MgCl_2$ solutions. Based on the binary parameters $\beta^{(0)}_{Th^{4+}/Cl^-} = 1.092$, $\beta^{(1)}_{Th^{4+}/Cl^-} = 13.7$, $\beta^{(2)}_{Th^{4+}/Cl^-} = -160$, and $C^{\phi}_{Th^{4+}/Cl^-} = -0.112$ from [1992ROY/VOG], Rai *et al.* [1997RAI/FEL] described the solubility of ThO_2(am, hyd) in NaCl and $MgCl_2$ solutions with the ternary parameters $\theta_{Th^{4+}/Na^+} = 0.42$, $\psi_{Th^{4+}/Na^+/Cl^-} = 0.21$ and $\theta_{Th^{4+}/Mg^{2+}} = 0.60$, $\psi_{Th^{4+}/Mg^{2+}/Cl^-} = 0.21$, respectively. The equilibrium constant for the reaction:

$$ThO_2(am, hyd) + 2H_2O(l) \rightleftharpoons Th^{4+} + 4OH^-$$

evaluated without taking hydrolysis reactions into account is $\log_{10} K^{\circ}_{s,0} = -45.5$ ($\log_{10} {}^{*}K^{\circ}_{s,0} = 10.5$), nearly the same as found in [1987RYA/RAI]. The uncertainty has not been estimated. Felmy *et al.* [1991FEL/RAI] tried to fit the solubility data by including also hydrolytic species, but without success. It is very difficult to estimate both equilibrium constants and Pitzer parameters even from very precise experimental data.

The fit between the thermodynamic model used and the experimental data varies; it is good in 0.1 M $NaClO_4$, in 0.6 M NaCl and at the high NaCl and $MgCl_2$ concentrations studied in [1997RAI/FEL]. In 1.2 and 3.0 M NaCl the fitted function deviates significantly and systematically from most experimental data.

As Th(IV) hydroxide complexes are not included in the models proposed in [1991FEL/RAI] and [1997RAI/FEL], the solubility and hydrolysis constants selected in this review must not be combined with the Pitzer parameters used by Rai *et al.* [1997RAI/FEL] for the Th^{4+} ion and vice versa −the solubility constants given in [1997RAI/FEL], [2000RAI/MOO] must not be combined with the SIT coefficients and hydolysis constants evaluated in the present review.

The experimental data of [1991FEL/RAI] and [1997RAI/FEL] have been re-evaluated using the hydrolysis constants and SIT coefficients selected in the present review. The values of $\log_{10} {}^{*}K^{\circ}_{s,0}$ and $\log_{10} K^{\circ}_{s,4}$ obtained from the solubility data are summarised in Table A-64. The corresponding values obtained from the study of [1987RYA/RAI] in 0.1 M $NaClO_4$ and a later study of this group in 0.1 M NaCl [2000RAI/MOO] are included for comparison. The solubility curves calculated with these "best fit" values of $\log_{10} {}^{*}K^{\circ}_{s,0}$ and $\log_{10} K^{\circ}_{s,4}$ are shown as dashed lines in Figure A-34. With the exception of the high $\log_{10} {}^{*}K^{\circ}_{s,0}$ value derived from solubility data in 0.1 M NaCl [2000RAI/MOO] and the high $\log_{10} K^{\circ}_{s,4}$ value derived from the widely scattered data in 3.0 M NaCl, the values recalculated to zero ionic strength are reasonably consistent, even those which were recalculated from the solubility data in 1.8 and 3.0 m $MgCl_2$ solutions, outside the validity range of the SIT. The mean values derived from the studies in 0.6−3.2 m NaCl [1991FEL/RAI], $\log_{10} {}^{*}K^{\circ}_{s,0} = (9.3 \pm 0.6)$ and $\log_{10} K^{\circ}_{s,4} = -(7.9 \pm 1.0)$ corresponding to $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.2 \pm 1.2)$ and the mean value derived from the data at pH < 6 in 4.0 and 6.0 m NaCl and in 1.0 m $MgCl_2$, $\log_{10} {}^{*}K^{\circ}_{s,0} = (8.4 \pm 0.7)$, are in the range of the equilibrium constants derived from other solubility studies with ThO_2(am, hyd), but the origin of the difference between the $\log_{10} {}^{*}K^{\circ}_{s,0}$ values from [1991FEL/RAI] and [1997RAI/FEL] is not clear. Both values are considered in the selection of thermodynamic data.

Table A-64: Equilibrium constants $\log_{10} {}^*K^\circ_{s,0}$ and $\log_{10} K^\circ_{s,4}$ at zero ionic strength re-evaluated by this review from solubility studies of [1991FEL/RAI], [1997RAI/FEL] with ThO_2(am, hyd) at room temperature. The values derived from [1987RYA/RAI], [2000RAI/MOO] are added for comparison. The results were assumed by this review to be valid for 298.15 K.

Reference	Medium	$\log_{10} {}^*K^\circ_{s,0}$	$\log_{10} K^\circ_{s,4}$
[1987RYA/RAI]	0.1 M $NaClO_4$	8.8 ± 0.5	−8.8 ± 0.4
[2000RAI/MOO]	0.1 M NaCl	9.8 ± 0.3	
[1991FEL/RAI]	0.6 M NaCl/KCl	9.4 ± 0.6	−8.3 ± 1.0
	1.2 M NaCl	9.3 ± 0.6	−8.1 ± 0.9
	3.0 M NaCl	9.2 ± 0.7	−7.4 ± 1.0
[1997RAI/FEL]	4.0 m NaCl	8.3 ± 0.7	
	6.0 m NaCl	8.1 ± 0.7	
	1.0 m $MgCl_2$	8.8 ± 0.4	
	1.8 m $MgCl_2$	7.8 ± 0.8 [a]	
	3.0 m $MgCl_2$	8.0 ± 0.7 [a]	

a: Ionic media far outside the validity range of the SIT.

Figure A-34: Solubility data determined by Rai *et al.* with ThO_2(am, hyd) at I = 0.1 M [1987RYA/RAI], [2000RAI/MOO], in 0.6 – 6.0 m NaCl and in 1.0 – 3.0 m $MgCl_2$ [1991FEL/RAI], [1997RAI/FEL]. The solid lines (——) are calculated with the hydrolysis constants and SIT coefficients selected by this review and $\log_{10} {}^*K^\circ_{s,0}$ = (8.5 ± 0.9) selected for ThO_2(am, aged, hyd). Dashed lines (– – –): Best fit at the corresponding ionic strength yielding the $\log_{10} {}^*K^\circ_{s,0}$ and $\log_{10} K^\circ_{s,4}$ values given in Table A-64.

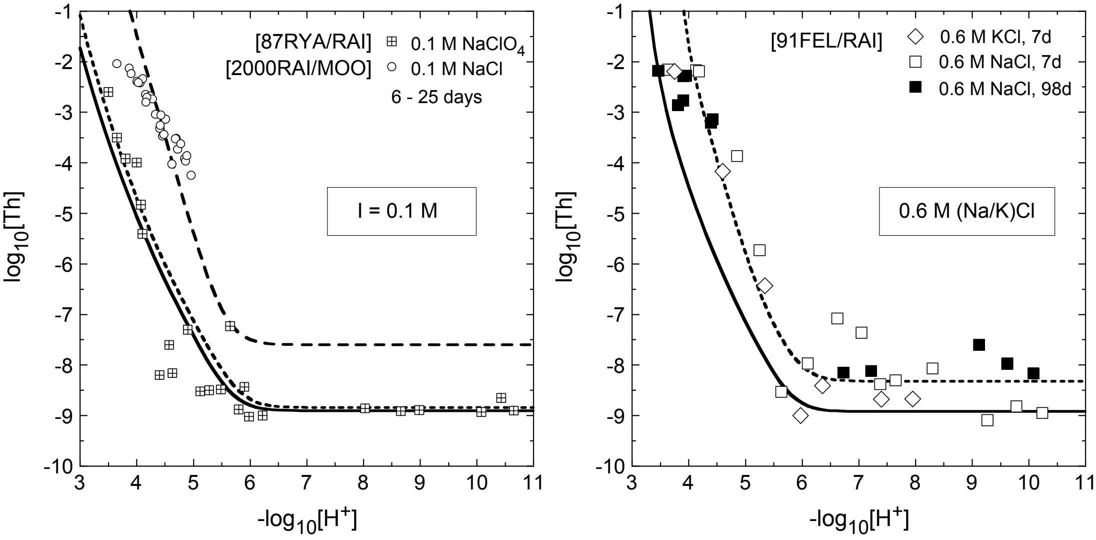


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Figure A-34 (continued)

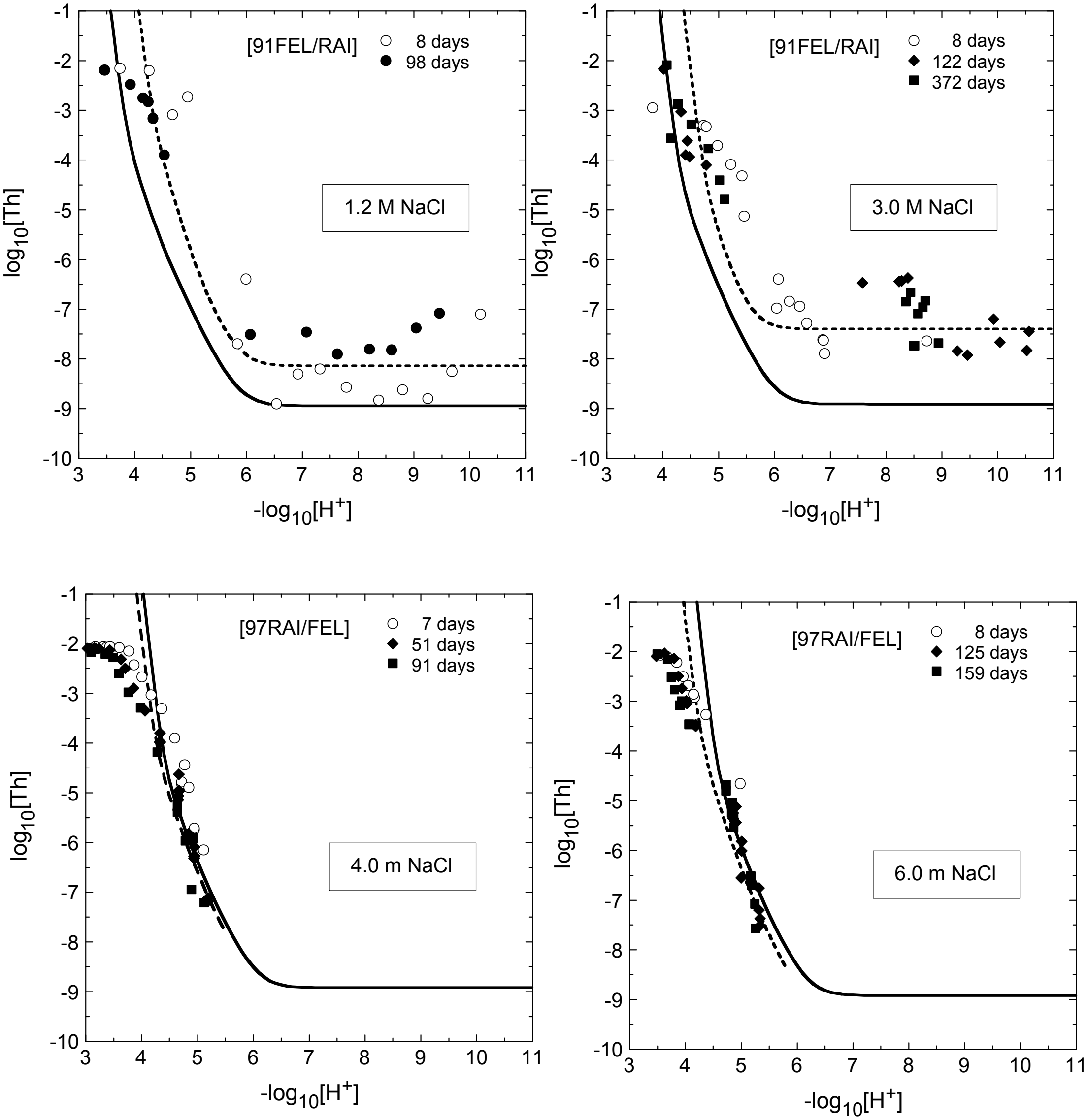

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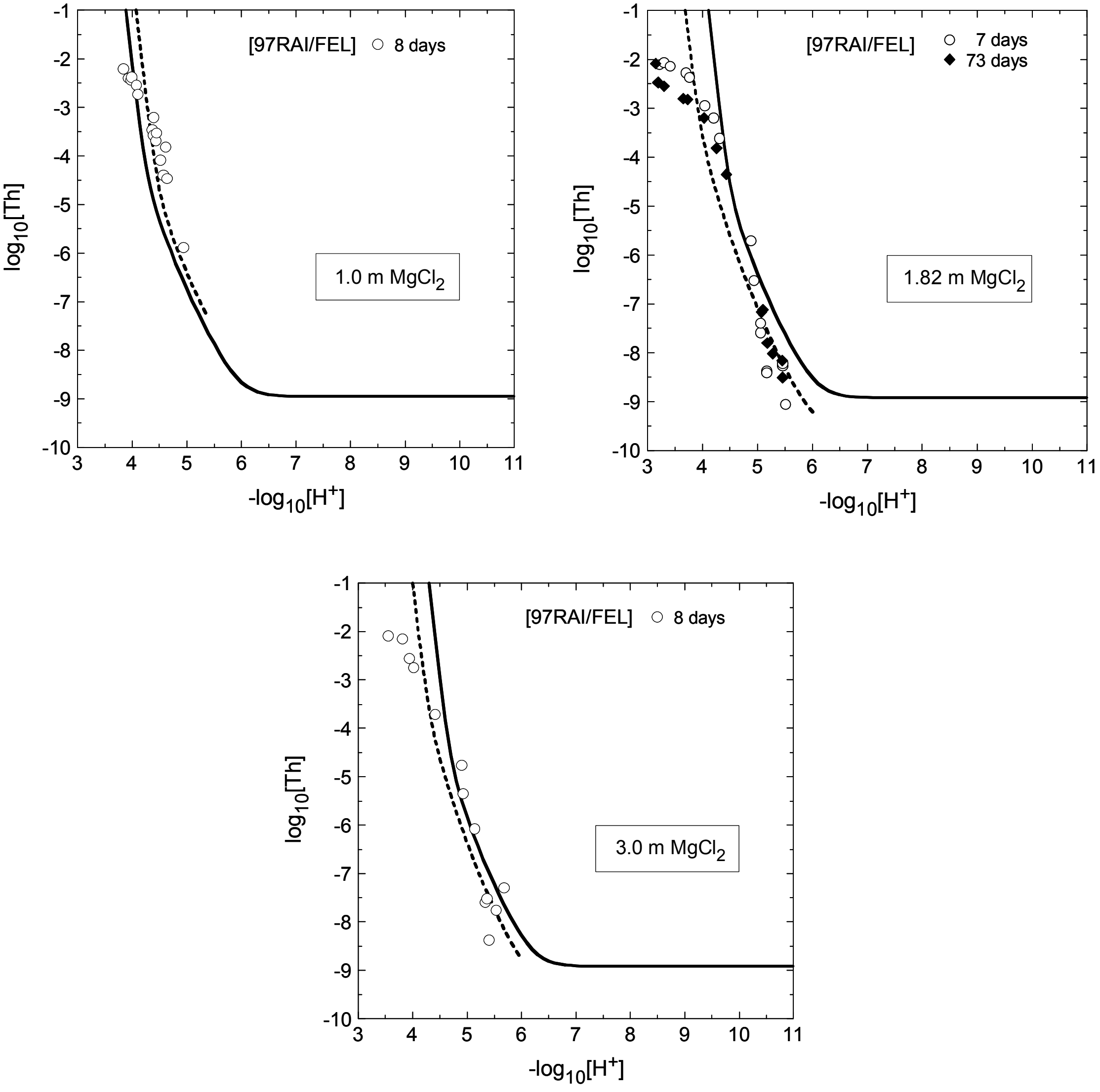
Figure A-34 (continued)



Effect of ageing on the solubility constant

The solubility data determined by [1991FEL/RAI] and [1997RAI/FEL] at pH < 5 in 3 − 6 m NaCl after relatively short equilibration time (< 10 days, open points) and after more than 70 days (filled points) clearly indicate ageing effects. The solubility data for fresh and aged ThO_2(am, hyd) give the solubility constants in Table A-65. The low Th concentrations at pH > 6, show no dependence on equilibration time.

The effect of ageing of ThO_2(am, hyd) precipitates may be interpreted in terms of increasing particle size *via* dissolution-precipitation equilibria, so called Ostwald ripening. This effect is kinetically favoured at higher aqueous Th concentrations, *i.e.*, at low pH.

The mean values of $\log_{10}{}^{*}K^{\circ}_{s,0}$ derived from the solubility data measured after equilibration for more than 70 days, $\log_{10}{}^{*}K^{\circ}_{s,0} = (9.1 \pm 0.4)$ (from [1991FEL/RAI]), and (8.1 ± 0.6) (from [1997RAI/FEL]), are included in the selection of data for ThO_2(am, aged, hyd). The corresponding solubility curves calculated with the selected solubility constant of $\log_{10}{}^{*}K^{\circ}_{s,0}$ (ThO_2(am, aged, hyd) = (8.5 ± 0.9) and the selected hydrolysis constants and SIT coefficients are shown as solid lines in Figure A-34.

Table A-65: Solubility constants $\log_{10}{}^{*}K^{\circ}_{s,0}$ at zero ionic strength re-evaluated from solubility studies of [1991FEL/RAI], [1997RAI/FEL] with fresh and aged ThO_2(am, hyd).

Reference	Medium	$\log_{10}{}^{*}K^{\circ}_{s,0}(ThO_2$(am, hyd))	
		Fresh (< 10 days)	Aged (> 70 days)
[1991FEL/RAI]	0.6 M NaCl/KCl	(9.5 ± 0.5)	(9.1 ± 0.4)
	1.2 M NaCl	(9.5 ± 0.7)	(9.2 ± 0.4)
	3.0 M NaCl	(9.8 ± 0.4)	(8.9 ± 0.5)
[1997RAI/FEL]	4.0 m NaCl	(8.6 ± 0.5)	(8.2 ± 0.5)
	6.0 m NaCl	(8.4 ± 0.6)	(8.0 ± 0.6)
	1.0 m $MgCl_2$	(8.8 ± 0.4)	

[1991GRE/LAG2]

This is a potentiometric study conducted in a 3.0 M $NaClO_4$ ionic medium at 25°C. The binary Th(IV)-OH^- system was investigated first and the ternary Th(IV)-OH^-- CO_3^{2-} system was then studied at two different partial pressures of CO_2(g), 0.29 bar (in N_2(g)) and 0.97 bar. The experiments are described in detail with the primary experimental data listed.

The main part of the study concerns the hydrolysis of Th(IV). The total Th(IV) concentrations used in these studies were 0.275, 0.535, 0.612, 1.066, 2.640 and 6.966 mM and the values of $-\log_{10}[H^+]$ covered a range of 2.5 to 4.1. Six different chemical models were tested against the experimental data using a least-squares program (LETAGROP) where the difference between experimental and calculated emf was minimised. The authors note that all of the solutions contain a large number of complexes, some of which are present in small amounts. All models give a small standard deviation in the error-carrying variable (the measured potential), at most 0.7 mV, corresponding to a standard deviation of 0.01 in $-\log_{10}[H^+]$. The two best models (Model 1 and Model 2), are given in Table A-66.

Table A-66: Equilibrium constants, $-\log_{10}{}^*\beta_{n,m}(Th_m(OH)_n^{4m-n})$ ±3σ in 3 M $NaClO_4$ and the standard deviation in the error-carrying variable *E* (in mV) from the least squares analysis of experimental data for the Th(IV)-hydroxide system. *U* is the error square sum for the different models.

$(n,m) = Th_m(OH)_n^{4m-n}$	Model 1	Model 2
$(1,1) = ThOH^{3+}$	4.35 ± 0.09	4.06 ± 0.07
$(3,1) = Th(OH)_3^+$	12.3 ± 0.2	-
$(4,1) = Th(OH)_4(aq)$	16.65 ± 0.04	16.58 ± 0.07
$(2,2) = Th_2(OH)_2^{6+}$	5.10 ± 0.17	5.1 ± 0.2
$(3,2) = Th_2(OH)_3^{5+}$	7.87 ± 0.05	-
$(8,4) = Th_4(OH)_8^{8+}$	19.6 ± 0.2	19.17 ± 0.08
$(12,4) = Th_4(OH)_{12}^{4+}$	34.86 ± 0.05	34.89 ± 0.10
$(14,6) = Th_6(OH)_{14}^{10+}$	33.67 ± 0.05	-
$(15,6) = Th_6(OH)_{15}^{9+}$	-	37.57 ± 0.09
$(16,6) = Th_6(OH)_{16}^{8+}$	42.9 ± 0.4	-
σ(EMF)/mV	0.42	0.70
U(EMF)/(mV)^2	17.27	45.03

The authors selected Model 1, but point out that one can remove species (16,6) and (3,1) without a large changes in the error square sum; this does not change the values of the remaining equilibrium constants within their estimated errors. It is difficult to decide between Models 1 and 2 using even these precise data. Two stoichiometries of the hexanuclear complexes ($Th_6(OH)_{15}^{9+}$ or $Th_6(OH)_{14}^{10+}$ with minor amounts of $Th_6(OH)_{16}^{8+}$) have been suggested in previous studies and the final choice is discussed in the main text (Section VII.3.4.1.4). The present review concludes that there is good evidence for the formation of the following complexes and equilibrium constants:

$Th(OH)^{3+}$ $\log_{10}{}^*\beta_{1,1} = -(4.2 \pm 0.15)$

$Th_2(OH)_2^{6+}$ $\log_{10}{}^*\beta_{2,2} = -(5.1 \pm 0.2)$

$Th_4(OH)_8^{8+}$ $\log_{10}{}^*\beta_{8,4} = -(19.4 \pm 0.2)$

$Th_4(OH)_{12}^{4+}$ $\log_{10}{}^*\beta_{12,4} = -(34.9 \pm 0.1)$.

These values are accepted by the present review and are included in the evaluation of selected data.

Four of the titrations were made with a total concentration of Th(IV) less than 0.001 M where the formation of a precipitate of hydrous oxide is minimised. However the data at $-\log_{10}[\mathrm{H}^+] > 3.8$ may be influenced by the formation of a precipitate even if none was observed experimentally. The complex $\mathrm{Th(OH)_4(aq)}$ is formed at the highest values of $-\log_{10}[\mathrm{H}^+]$ and the proposed equilibrium constant is not accepted by this review.

The experimental studies of the carbonate system were made at two different partial pressures of $\mathrm{CO_2(g)}$ (0.29 and 0.97 atm.). The experimental values of $\bar{Z}\,(\log_{10}[\mathrm{H}^+])$, where $\bar{Z}$ is the average number of protons formed in the reactions, change dramatically from those in the binary Th(IV)-$\mathrm{OH^-}$ system, clearly demonstrating that carbonate complexes are formed. However it was not possible to analyse the experimental data in terms of a unique chemical model. Grenthe and Lagerman noticed that the very steep $\bar{Z}\,(\log_{10}[\mathrm{H}^+])$ curves might indicate the formation of complexes with high nuclearity. The proposed complexes are "$\mathrm{Th_8(OH)_{24}(CO_2)_2^{8+}}$" ≡ $\mathrm{Th_8(OH)_{20}(CO_3)_2^{8+}}$ and "$\mathrm{Th_{16}(OH)_{52}(CO_2)_{16}^{12+}}$" ≡ $\mathrm{Th_{16}(OH)_{20}(CO_3)_{16}^{12+}}$; they might be formed through linking of hydroxide complexes by carbonate bridges. However, this review agrees with [1991GRE/LAG2] that is not possible to deduce a unique chemical model from these data. The formation of large ternary complexes is confirmed by a comparison of the solubility studies of Östhols *et al.* [1994OST/BRU] in 0.5 M $\mathrm{NaClO_4}$ and Altmaier *et al.* [2005ALT/NEC] in 0.5 M NaCl, both studies performed with $\mathrm{ThO_2(am, hyd)}$ under $\mathrm{CO_2}$ partial pressures of 1.0 and 0.1 bar. The data of Östhols *et al.* [1994OST/BRU] in the region of minimum solubility at pH 4.5 – 6.5, determined after 300 nm filtration, are considerably higher than those of Altmaier *et al.* [2005ALT/NEC], where large complexes were removed by 1.2 nm ultrafiltration and ultracentrifugation at 5×10^5 g. For the test solutions with the lowest total concentration of Th(IV), the steep rise in the $\bar{Z}$-curves occurs at $-\log_{10}[\mathrm{H}^+]$ around 3.3, where there should be no precipitation of Th(IV) hydrous oxide and no significant formation of carbonate complexes according to Figure XI-2; the potentiometric and the solubility data are not consistent. A possible explanation suggested by this review might be that hydrous oxides precipitate on the $\mathrm{CO_2}$ gas-bubbles.

[1991JOH/MAG]

The coordination around Th(IV) in aqueous perchlorate, chloride and nitrate solutions has been determined using large angle X-ray scattering (LAXS) data. The total concentration of Th(IV) in the various test solutions range from approximately 1 to 2.5 molal; the concentrations of perchlorate from 5 – 11 m; the concentration chloride from 4 – 7 m and nitrate from 4.4 – 10 m. At these high total concentrations of electrolytes the water activity is significantly different from unity. The hydrogen ion concentration in the test solutions is sufficiently high to prevent hydrolysis.

The data in perchlorate solutions indicates that perchlorate is not coordinated and that the first coordination sphere contains (8.0 ± 0.5) coordinated water ligands with a bond distance Th–OH_2 of 2.48 Å; the perchlorate ions seems to be located in the second coordination sphere, presumably linked by hydrogen bonding and electrostatic interactions to the first sphere. The coordination number in the chloride system is 10.5, with indications of chloride entering the first coordination sphere. One would not expect that coordination of chloride should result in an increase of the coordination number and the difference observed probably indicates the uncertainty in the determination of coordination numbers using LAXS. The LAXS data from nitrate solutions indicate that inner-sphere nitrate complexes are formed and that these are stronger than chloride complexes. The nitrate ligand seems to be bi-dentate coordinated, as in most crystal structures and the coordination number is larger than eight, indicating that several nitrate ligands are coordinated at the high nitrate concentrations used.

[1991MAR2]

This paper describes an empirical electrostatic model for the estimation of the Gibbs energy of hydration of ions. [1987MAR] is a publication with a similar topic but this was not available to the reviewers. We assume that the later study [1991MAR2] is based on the previous one. The key parameters in the model are the charge and "corrected" ionic radii of the ions. The physico-chemical model consists of two parts: the ion with a layer of n water molecules that are considered rigid and subject to electrostriction and a second layer with the same properties as the bulk solvent. The number of water molecules is determined by an empirical fitting using the relationship $n = A|Z|/r$, where A is an empirical parameter. There is no reason to expect that this simplistic expression should give a proper description of the inner coordination sphere of ions. For Th^{4+} the value of n is 14.4, in poor agreement with experimental observations. The correction to the ionic radius, Δr, is a measure of the thickness of the "rigid" layer of water surrounding the hydrated ion; this quantity is also determined by a fitting procedure. The fitted parameters involve a comparison of experimental and calculated Gibbs energy of hydration, $\Delta_{\text{hyd}}G^{\circ}_{\text{m}}$; the result is listed in Table 1 of [1991MAR2]. For thorium the result is $\Delta_{\text{hyd}}G^{\circ}_{\text{m}}$ (calc) = −5395 kJ·mol^{-1} and $\Delta_{\text{hyd}}G^{\circ}_{\text{m}}$ (exp) = −5815 kJ·mol^{-1}. It is of interest to compare these values with the data given by Yang *et al.* [2001YAN/TSU] in their Table 1. They find a difference in binding energy between gas phase and solvent equal to 2663 kJ·mol^{-1} for $Th(H_2O)_9^{4+}$ with slight variations between different geometries (15 kJ·mol^{-1}); the corresponding solvation energy for $Th(H_2O)_{10}^{4+}$ is 2709 kJ·mol^{-1}. These values indicate that the structure of the first coordination sphere affects the hydration energy, an effect that is not taken into account in models of the type used by Marcus. The difference in hydration energy between the empirical and the quantum mechanical model is a factor of about two and it is difficult to judge the reason for this; however one should notice that $\Delta_{\text{hyd}}G^{\circ}_{\text{m}}$ (exp) is not obtained directly but involves a number of extra-thermodynamic assumptions. This review does not consider the Gibbs energy of hydration of Th^{4+} as reliable; however the relative values of the Gibbs energy of solvation listed in Table 1 of [1991MAR2] are probably more reliable than their absolute values.

[1992BIS/KRA]

This paper contains no quantitative information on thorium complexes. The authors note that solubility experiments on hydrous thorium oxide did not reach equilibrium after 2 months and that the only experimental data they have obtained refer to a "quasi-solubility" curve obtained after equilibration for ten days. There is no other useful information for this review.

[1992BLA/WYA]

This report is a comprehensive collection of the energy levels of the gaseous atoms and ions of all the actinide elements. The listing for Th(g) contains 693 energy levels, the highest level being at 46844 cm^{-1}, 2156 cm^{-1} below the ionisation level, (49000 ± 1000) cm^{-1}.

These data have been utilised to calculate S°_{m} (Th, g, 298.15 K) = (190.170 ± 0.010) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $C^{\circ}_{p,\text{m}}$ (Th, g, 298.15 K) = (20.790 ± 0.005) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The calculated heat capacities at higher temperatures have been fitted four-term equations as a function of T.

The uncertainties have been estimated by this review.

[1992ENG/ALB]

The authors have used liquid-liquid extraction to investigate the hydrolysis of Th(IV) and the complex formation with acetylacetone, which transfers Th(IV) from an aqueous to a toluene phase. The experiments have been made at 25°C in a 1 M NaClO_4 ionic medium over the pH range 1 − 11. The pH was measured using a glass-electrode calibrated with standard buffers; hence the reported equilibrium constants are not concentration constants but "mixed" equilibrium constants. The authors mention neither the electrode system used for pH measurements, nor how they converted measured pH values into $\log_{10}[\text{H}^+]$ or $\log_{10}[\text{OH}^-]$. They mention that no corrections were made for different liquid junction potentials during calibration and 1.0 M NaClO_4 test solutions. Depending on the electrode type and junction electrolyte used, this can lead to large errors for up to 0.3 units in $\log_{10}[\text{H}^+]$. With the exception of these shortcomings, the experimental method used is satisfactory; the measured distribution coefficients are not dependent on sorption of Th(IV) on the container walls. The analysis of the data is less satisfactory, the proposed equilibrium constants have large uncertainties and do not describe the experimental data except in certain regions; it is obvious to this review that the chemical model is incomplete.

The measured distribution coefficient, D_{M}, is equal to:

$$D_M = \frac{\lambda_4\,\beta_{140}[\mathrm{L}]^4}{1+\sum\limits_1^n \beta_{1n0}[\mathrm{L}]^n + \sum\limits_1^p \beta_{10p}[\mathrm{OH}]^p} \qquad \text{(A.82)}$$

where the equilibrium constant for the reaction:

$$m\mathrm{Th}^{4+} + n\mathrm{L}^- + p\mathrm{OH}^- \rightleftharpoons \mathrm{Th}_m\mathrm{L}_n(\mathrm{OH})_p^{4m-n-p}$$

is

$$\beta_{m,n,p} = \frac{[\mathrm{Th}_m\mathrm{L}_n(\mathrm{OH})_p^{4m-n-p}]}{[\mathrm{Th}^{4+}]^m[\mathrm{L}]^n[\mathrm{OH}]^p}\,; \qquad \text{(A.83)}$$

HL is acetylacetone, and L^- the corresponding anion, the concentration of which can be calculated as shown in Eq. (A.84),

$$[\mathrm{L}^-] = \frac{K_a\left[\mathrm{HL}\right]_{\mathrm{org}}}{\left[\mathrm{H}^+\right](1+K_d+K_a\left[\mathrm{H}^+\right]^{-1})}\,; \qquad \text{(A.84)}$$

D_M is the measured distribution coefficient for M = Th between the organic and aqueous phases, λ_4 the distribution coefficient of the uncharged complex $\mathrm{ThL_4}$, K_a the dissociation constant of HL and K_d the distribution coefficient for HL between 1 M $\mathrm{NaClO_4}$ and toluene.

The reported equilibrium constants are given in Table A-67.

Table A-67: Equilibrium constants for Th(IV) hydroxide and acetylacetonate complexes at 25°C in 1 M $\mathrm{NaClO_4}$. The distribution coefficient K_d(HL) between toluene and water is 3.23. The value of λ_4 is 427.

Complex	$\log_{10}\beta_{m,n,p}$
ThL^{3+}	$\log_{10}\beta_{1,1,0} = 8.2 \pm 0.6$
ThL_2^{2+}	$\log_{10}\beta_{1,2,0} = 15.4 \pm 0.6$
ThL_3^{+}	$\log_{10}\beta_{1,3,0} = 22.6 \pm 1.9$
$\mathrm{ThL_4}$	$\log_{10}\beta_{1,4,0} = 25.8 \pm 1.2$
$\mathrm{Th(OH)}^{3+}$	$\log_{10}\beta_{1,0,1} = 9.1 \pm 3.1$
$\mathrm{Th(OH)}_2^{2+}$	$\log_{10}\beta_{1,0,2} = 19.0 \pm 2.7$
$\mathrm{Th(OH)}_3^{+}$	$\log_{10}\beta_{1,0,3} = 26.2 \pm 2.9$
$\mathrm{Th(OH)_4(aq)}$	$\log_{10}\beta_{1,0,4} = 33.1 \pm 3.0$
L^-	$\log_{10}K_\mathrm{a} = -9.0$

The total concentration of Th is low, 0.1 mM, indicating that mononuclear complexes are favoured; however, previous potentiometric data indicate that polynuclear complexes still play an important role at this low concentration. From Eq. (A.82) it is apparent that the authors have not taken the possible formation of ternary complexes into account. As the primary experimental data are only given in the rather small figures we have not been able to reanalyse them. However, the large uncertainty in the reported equilibrium constants and the neglect of ternary and polynuclear complexes makes the constants proposed unreliable.

[1992EWA/SMI]

Ewart *et al.* [1992EWA/SMI] studied the solubilities of thorium, protactinium, uranium, neptunium, plutonium, and americium, presumably at room temperature (*ca.* 22°C) under conditions representative of a cementitious near-field environment. The solubility of $Th(OH)_4(s)$ in water pre-equilibrated with 1:3 ordinary Portland cement / blast furnace sludge plus limestone aggregate ($I \approx 0.03$ M) was measured from oversaturation at $[Th]_{tot} = 10^{-4}$ M by adding an aliquot of $ThCl_4$ stock solution and adjusting pH in the range of 8 – 13. The experiments were performed in a nitrogen glove box. The thorium concentrations analysed by ICP-MS after 25000 – 30000 MWCO (Molecular Weight Cut-Off) (*ca.* 2 – 4 nm) ultrafiltration were in the range $(4 \pm 2) \times 10^{-9}$ M, independent of pH. Equilibration time and pH measurement are not reported in this paper, but the results are comparable to those of other authors [1989MOO], [1987RYA/RAI], [1991FEL/RAI], [2002NEC/MUL].

[1992FEL/RAI]

The study was undertaken to develop a reliable thermodynamic model for thorium sulphate systems extending from dilute to concentrated electrolytes (Li_2SO_4, NH_4SO_4, Na_2SO_4, K_2SO_4, H_2SO_4) in order to account for strong ion-interactions or complex formation that can occur for these electrolytes in dilute solution. Extensive use was made of the solvent extraction data reported by [1963ALL/MCD] and of the solubility data summarised in [1965LIN2] to develop a comprehensive thermodynamic model using the Pitzer approach. The model developed in this study included 1) Pitzer ion-interaction parameters for Th^{4+} with sulphate and bisulphate and for $Th(SO_4)_3^{2-}$ with the bulk electrolyte cations, and 2) molar Gibbs energies of formation of aqueous species ($Th(SO_4)_2(aq)$ and $Th(SO_4)_3^{2-}$) and for several $Th(SO_4)_2{\cdot}xH_2O$ (x = 4, 8, or 9) solids and double salts of $Th(SO_4)_2$ with Na_2SO_4, K_2SO_4, and $(NH_4)_2SO_4$. The Pitzer ion-interaction parameters and $\Delta_f G_m^\circ/RT$ values for all of the species used in the model are listed in the Table A-68 and Table A-69 given below. Temperature-corrected Pitzer ion-interaction parameter values, the chemical potential of water and A^φ, a Debye-Hückel term, were used to correct for temperature effects. The predictions by this model provided close agreement with extensive reliable experimental solvent extraction and solubility data [1965LIN2] extending from dilute to concentrated electrolytes. In addition to the values reported for various solids, the authors show that the $\Delta_f G_m^\circ$ value listed by [1982WAG/EVA] for $Th(SO_4)_2(cr)$ most likely is in error.

Table A-68: Ion interaction (Pitzer) parameters given in [1992FEL/RAI].

Binary interactions

Cation	Anion	$\beta^{(o)}$ (kg·mol^{-1})	$\beta^{(1)}$ (kg·mol^{-1})	$\beta^{(2)}$ (kg·mol^{-1})	C^{φ} (kg^{2}·mol^{-2})
Na^+	SO_4^{2-}	0.01958	1.113	—	0.00497
Na^+	HSO_4^-	0.0454	0.398	—	—
Na^+	OH^-	0.0864	0.253	—	0.0044
Na^+	$Th(SO_4)_3^{2-}$	0.12	—	—	—
K^+	SO_4^{2-}	0.04995	0.7793	—	—
K^+	$Th(SO_4)_3^{2-}$	0.90	—	—	—
Li^+	SO_4^{2-}	0.136	1.27	—	–0.00406
Li^+	$Th(SO_4)_3^{2-}$	0.52	—	—	—
Th^{4+}	SO_4^{2-}	1.56	—	—	—
Th^{4+}	HSO_4^-	1.44	—	—	—
Th^{4+}	Cl^-	1.014	13.3	–200	–0.103
H^+	SO_4^{2-}	0.0298	—	—	0.0438
H^+	HSO_4^-	0.2065	0.5556	—	—
H^+	$Th(SO_4)_3^{2-}$	0.84	—	—	—
NH_4^+	$Th(SO_4)_3^{2-}$	0.26	—	—	—

Neutral species	Anion	λ (kg·mol^{-1})
$Th(SO_4)_2(aq)$	HSO_4^-	0.68
$Th(SO_4)_2(aq)$	Cl^-	0.29

Ternary interactions

Cation	Cation	Anion	θ_{cc} (kg·mol^{-1})	ψ_{cca} (kg^{2}·mol^{-2})
NH^{4+}	Th^{4+}	SO_4^{2-}	−0.44	0.06
H^+	Th^{4+}	Cl^-	0.60	0.08

Table A-69: Dimensionless molar Gibbs energies of formation at 25°C unless otherwise identified (from [1992FEL/RAI]).

Species	Temperature (ºC)	$\Delta_f G_m / RT$
$H_2O(l)$	16	– 96.375
$H_2O(l)$		– 95.6635
$H_2O(l)$	30	– 95.297
SO_4^{2-}		– 300.386
Th^{4+}		– 284.227
$Th(SO_4)_2(aq)$		– 911.69
$Th(SO_4)_3^{2-}$		– 1214
$Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(s)$	16	– 2011.29
$Th(SO_4)_2{\cdot}(NH_4)_2SO_4{\cdot}4H_2O(s)$	16	– 1668.39
$Th(SO_4)_2{\cdot}2(NH_4)_2SO_4{\cdot}2H_2O(s)$	16	– 1841.41
$Th(SO_4)_2{\cdot}3(NH_4)_2SO_4{\cdot}3H_2O(s)$	16	– 2303.52
$Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(s)$	16	– 1837.57
$Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(s)$	16	– 2181.81
$Th(SO_4)_2{\cdot}3.5K_2SO_4(s)$	16	– 2790.83
$Th(SO_4)_2{\cdot}9H_2O(s)$		– 1775.9
$Th(SO_4)_2.{\cdot}9H_2O(s)$	16	– 1782.38
$Th(SO_4)_2{\cdot}8H_2O(s)$		– 1680
$Th(SO_4)_2{\cdot}8H_2O(s)$	30	– 1677.07
$Th(SO_4)_2{\cdot}4H_2O(s)$	30	– 1294.13

The $\Delta_f G_m^o / RT$ values of Th species, along with the values for auxiliary species reported by the authors, were used to calculate equilibrium constants for reactions involving thorium sulphate compounds and complexes (Table A-70). The literature data used by [1992FEL/RAI] formed the basis for developing a model based on SIT parameters. For these interpretations the SIT parameters reported in Table IX-2 and the values of β_1^o, β_2^o, and β_3^o selected in this review (Table IX-1) were used in the NONLINT-SIT program to determine the solubility products of various hydrated thorium sulphates. The details of these calculations are discussed in the text sections IX.1.3.3 and IX.1.3.4. The solubility products reported in Table A-70 are on an average about 1.9 $\log_{10}$-units lower than the solubility products calculated by this review with the SIT model (see Table IX-4). This is primarily a result of differences in the $\log_{10} \beta_2^o$ and $\log_{10} \beta_3^o$ values of (9.69 ± 0.27) and (10.748 ± 0.076) with the SIT model and of 11.592 and 12.427 used by [1992FEL/RAI] for $Th^{4+} + n\,SO_4^{2-} \rightleftharpoons Th(SO_4)_n^{4-2n}$. It should be noted that apart from these differences the fits to experimental data are equally good with both models, in the ionic strength range where the SIT model is applicable.

Table A-70: Equilibrium constants of reactions involving thorium sulphate compounds and complexes. The values are based on the Pitzer model and the $\Delta_f G^o_m/RT$ values presented in [1992FEL/RAI].

Reaction	Temperature (ºC)	$\log_{10} K^o$
$Th^{4+} + 2\,SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)$		11.592
$Th^{4+} + 3\,SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$		12.427
$Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(s) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2\,Na^+ + 6\,H_2O$	16	– 15.788
$Th(SO_4)_2{\cdot}(NH_4)_2SO_4{\cdot}4H_2O(s) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2\,NH_4^+ + 4\,H_2O$	16	– 14.535
$Th(SO_4)_2{\cdot}2(NH_4)_2SO_4{\cdot}2H_2O(s) \rightleftharpoons Th^{4+} + 4\,SO_4^{2-} + 4\,NH_4^+ + 2\,H_2O$	16	– 15.088
$Th(SO_4)_2{\cdot}3(NH_4)_2SO_4{\cdot}3H_2O(s) \rightleftharpoons Th^{4+} + 5\,SO_4^{2-} + 6\,NH_4^+ + 3\,H_2O$	16	– 15.669
$Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(s) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2K^+ + 4\,H_2O$	16	– 16.838
$Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(s) \rightleftharpoons Th^{4+} + 4\,SO_4^{2-} + 4\,K^+ + 2\,H_2O$	16	– 20.612
$Th(SO_4)_2{\cdot}3.5K_2SO_4(s) \rightleftharpoons Th^{4+} + 5.5\,SO_4^{2-} + 7\,K^+$	16	– 24.660
$Th(SO_4)_2{\cdot}9H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 9\,H_2O$	25	– 12.998
$Th(SO_4)_2{\cdot}9H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 9\,H_2O$	16	– 13.031
$Th(SO_4)_2{\cdot}8H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 8\,H_2O$	25	– 12.896
$Th(SO_4)_2{\cdot}8H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 8\,H_2O$	30	– 12.896
$Th(SO_4)_2{\cdot}4H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 4\,H_2O$	30	– 12.135

[1992FUG/KHO]

This standard text on the chemical thermodynamics of actinide elements contains information on most of the inorganic complexes of Th(IV) that are discussed in the present critical review. As judged by the Introduction the authors have used the same principles of evaluation as in the present critical review to evaluate the equilibrium constants of aqueous inorganic complexes, with the difference that the Guggenheim equation

$$\log_{10}\beta_n = \log_{10}\beta_n^o + \Delta z^2 \frac{A\sqrt{\mu}}{1+\sqrt{\mu}} + B\mu$$

has been used to calculate the ionic strength dependence of the equilibrium constants. μ is the ionic strength, z the ionic charge, A the Debye-Hückel parameter and B a specific ion interaction parameter that is not identical with the corresponding parameter ε because of the different Debye-Hückel terms; there are no tabulations of the B parameters. The difference between the equilibrium constants at zero ionic strength calculated with the Guggenheim and SIT approaches is usually small. The analysis of the different experimental studies is not as well documented as in the NEA series and accordingly only the final outcome of the analysis can be compared with the ones obtained in the present review. These equilibrium constants are listed in the tables in the main chapter. For the important Th(IV)-hydroxide system the authors of [1992FUG/KHO] have not selected any constants at zero ionic strength. Equilibrium constants have been selected for the complexes ThF^{3+}, ThF_2^{2+}; $ThCl^{3+}$, $ThCl_2^{2+}$; $ThClO_3^{3+}$;

selected for the complexes ThF^{3+}, ThF_2^{2+} ; $ThCl^{3+}$, $ThCl_2^{2+}$; $ThClO_3^{3+}$; $ThBrO_3^{3+}$; $ThIO_3^{3+}$; $ThSO_4^{2+}$; $Th(SO_4)_2(aq)$; $Th(NO_3)_n^{4-n}$, $n = 1-4$; $Th(H_3PO_4)^{4+}$, $Th(H_2PO_4)^{3+}$, $Th(H_2PO_4)_2^{2+}$ $Th(H_3PO_4)(H_2PO_4)^{3+}$; $Th(CrO_4)^{2+}$. In addition there are discussions of complex formation in the following binary Th(IV) systems: N_3^-; HPO_4^{2-} ; $P_2O_7^{4-}$ and SCN^-. The corresponding experimental data are also discussed in the present review.

[1993ABE/GLA]

The authors have studied the tetranuclear complex "$Zr_4(OH)_8^{8+}$" in aqueous solution using NMR spectroscopy. Based on these data they suggest that the stoichiometry of the complex is $[Zr_4(OH)_8(OH_2)_8^{I}(OH_2)_8^{II}]^{8+}$, where $(OH_2)^{I}$ and $(OH_2)^{II}$ denote two different sites of the coordinated water that differ by their rate of exchange of protons with the bulk water. The authors also note the extremely slow rates of exchange of both water and hydroxide with the water solvent, a feature that is much more pronounced than in the less hydrolysed Th(IV).

[1993FEL/RAI]

The solubilities of a number of binary and ternary thorium fluorides were studied as a function of the concentrations of NaF and NH_4F. The original precipitate was formed by reacting thorium stock solution in 0.1 M HNO_3 with 0.1 M HF and portions of this precipitate was suspended in NaF and NH_4F solutions ranging in concentrations from 0.0001 M to 1.0 M. The suspensions were equilibrated over a period of about 3 months at room temperature (this review has assumed a temperature of (22 ± 2)°C). All equilibrated solids were found to be crystalline and characterised by XRD and total chemical analyses. The characterised solids in the NaF system included $ThF_4{\cdot}xH_2O(s)$, $ThF_4{\cdot}NaF{\cdot}H_2O(s)$, and $ThF_4{\cdot}3NaF(s)$, and those in the NH_4F system included $ThF_4{\cdot}xH_2O(s)$ and $ThF_4{\cdot}NH_4F(s)$. The aqueous phase concentrations were determined after filtration through ~ 0.0018 μm filters. The measured pH values were > 4.2 indicating that F^-, rather than HF(aq), is the important aqueous fluoride species. The data were interpreted using the Pitzer model. The values of $\Delta_f G_m^o / RT$ for ThF_3^+ and $ThF_4(aq)$ were calculated from the data given by [1982WAG/EVA]; other values, including the $\Delta_f G_m^o / RT$ values for $ThF_4{\cdot}xH_2O(s)$, $ThF_4{\cdot}NaF{\cdot}H_2O(s)$, $ThF_4{\cdot}NH_4F(s)$, ThF_5^-, and ThF_6^{2-} and the associated Pitzer ion-interaction parameters for the important species, were fitted. For reasons given in the discussion of these values in Section VIII.1.3, the proposed equilibrium constants based on the data of [1982WAG/EVA] have not been accepted. Although [1993FEL/RAI] do not list $\Delta_f G_m^o / RT$ values for ThF^{3+} and ThF_2^{2+}, they state that according to the data reported in [1982WAG/EVA], these species do not contribute significantly to the total thorium concentrations at the fluoride concentrations used in the experiments. The values of equilibrium constants determined from the $\Delta_f G_m^o / RT$ values and of the important Pitzer ion interaction parameters they report are given in the following tables.

Table A-71: Ion interaction parameters used by [1993FEL/RAI] in studies with thorium in NaF and NH_4F solutions.

Species	$\beta^{(0)}$ ($kg\cdot mol^{-1}$)	$\beta^{(1)}$ ($kg\cdot mol^{-1}$)	C^{φ} ($kg^2\cdot mol^{-2}$)
Na^+ -F^-	0.0215	0.2107	0.0
NH_4^+ -F^-	0.08089	0.2021	0.00093
NH_4^+ - ThF_6^{2-}	– 1.3	0.0	0.0

Table A-72: Equilibrium constants for different reactions based on the data in [1993FEL/RAI].

Reaction	$\log_{10} K^{\circ}$
$Th^{4+} + 3F^- \rightleftharpoons ThF_3^+$	18.891 [a]
$Th^{4+} + 4F^- \rightleftharpoons ThF_4(aq)$	22.239[a]
$Th^{4+} + 5F^- \rightleftharpoons ThF_5^-$	24.763 [b]
$Th^{4+} + 6F^- \rightleftharpoons ThF_6^{2-}$	25.562 [b]
$ThF_4\cdot xH_2O(cr) \rightleftharpoons Th^{4+} + 4F^- + xH_2O(l)$	–28.927 [b]
$ThF_4\cdot NaF\cdot H_2O(cr) \rightleftharpoons Th^{4+} + 5F^- + Na^+ + H_2O(l)$	–34.028 [b]
$ThF_4\cdot NH_4F(cr) \rightleftharpoons Th^{4+} + 5F^- + NH_4^+$	–33.888 [b]

a: Values from [1982WAG/EVA].

b: Uncertainty values are not reported by the authors, but they are far less than 0.2 in all cases

The study of [1993FEL/RAI] is the only source of data available for double salts and for the solubility of ThF_4(cr, hyd) in relatively dilute solutions where the fluoride accounts for the major portion of the total fluoride concentrations. This is also the only study conducted at relatively high fluoride concentrations where the anionic thorium fluoride complexes are shown to be important. The aqueous phase model selected in this review is significantly different from the aqueous phase model used by [1993FEL/RAI]. Therefore to obtain data for the double salts and the anionic thorium fluoride complexes, and to develop a comprehensive model consistent with all of the available information, it was necessary to reinterpret these data, as discussed in detail in Sections VIII.1.2 and VIII.1.3. Based on the thermodynamic data selected/fitted from [1993FEL/RAI] (Tables VIII-8 and VIII-9), comparisons of the observed [1993FEL/RAI] and predicted concentrations are presented in Figures VIII-3 and VIII-4 and in Table A-73 to Table A-76.

Table A-73: Experimental and predicted concentrations for the solubility of ThF_4(cr, hyd) at 25°C in NaF solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-3b.

Experimental concentrations (m)		Predicted concentrations (m)							
NaF $\times10^3$	Th $_{total}$ $\times10^7$	Th $_{total}$ $\times10^7$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	ThF_2^{6-}	F^- $\times10^3$
0.1720	9.052	7.235	0	3.187×10^{-12}	2.850×10^{-9}	4.990×10^{-8}	6.707×10^{-7}	8.562×10^{-11}	0.1684
0.1750	9.526	7.226	0	3.035×10^{-12}	2.758×10^{-9}	4.908×10^{-8}	6.707×10^{-7}	8.851×10^{-11}	0.1712
0.4990	6.466	6.892	0	1.437×10^{-13}	3.525×10^{-10}	1.734×10^{-8}	6.707×10^{-7}	7.620×10^{-10}	0.4964
0.4690	6.810	6.902	0	1.726×10^{-13}	3.986×10^{-10}	1.845×10^{-8}	6.707×10^{-7}	6.718×10^{-10}	0.4663
0.9410	5.690	6.829	0	0	1.044×10^{-10}	9.346×10^{-9}	6.707×10^{-7}	2.778×10^{-9}	0.9387
0.9620	5.690	6.829	0	0	9.998×10^{-11}	9.145×10^{-9}	6.707×10^{-7}	2.905×10^{-9}	0.9597
5.000	7.974	7.582	0	0	4.684×10^{-12}	1.902×10^{-9}	6.707×10^{-7}	8.555×10^{-8}	4.997
5.000	8.405	7.581	0	0	4.684×10^{-12}	1.902×10^{-9}	6.707×10^{-7}	8.554×10^{-8}	4.996
10.00	11.21	10.34	0	0	1.376×10^{-12}	1.003×10^{-9}	6.707×10^{-7}	3.627×10^{-7}	9.995
10.00	7.716	10.35	0	0	1.375×10^{-12}	1.003×10^{-9}	6.707×10^{-7}	3.628×10^{-7}	9.996

Table A-74: Experimental and predicted concentrations for the solubility of $ThF_4\cdot NaF\cdot H_2O$(cr) at 25°C in NaF solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-4a.

Experimental concentrations (m)		Predicted concentration (m)							
NaF$\times10^2$	Th $_{total}$$\times10^8$	Th $_{total}$$\times10^8$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	ThF_2^{6-}	$F^-$$\times10^2$
5.000	4.052	1.917	0	0	0	3.870×10^{-13}	1.073×10^{-9}	1.810×10^{-8}	5.000
5.000	4.095	1.917	0	0	0	3.870×10^{-13}	1.073×10^{-9}	1.810×10^{-8}	5.000
10.00	1.595	2.370	0	0	0	0	2.988×10^{-10}	2.340×10^{-8}	10.00
10.00	2.931	2.370	0	0	0	0	2.988×10^{-10}	2.340×10^{-8}	10.00
20.00	1.336	3.236	0	0	0	0	8.409×10^{-11}	3.228×10^{-8}	20.00
20.00	2.026	3.236	0	0	0	0	8.409×10^{-11}	3.228×10^{-8}	20.00

Table A-75: Experimental and predicted concentrations for the solubility of ThF_4(cr, hyd) at 25°C in NH_4F solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-3a.

Experimental concentrations (m)		Predicted concentrations (m)							
$NH_4F\times10^3$	$Th_{total}\times10^7$	$Th_{total}\times10^7$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	ThF_2^{6-}	$F^-\times10^3$
0.100	8.620	5.059	0	1.140×10^{-12}	1.279×10^{-9}	2.814×10^{-8}	4.764×10^{-7}	9.708×10^{-11}	0.2126
0.100	6.770	5.012	0	6.890×10^{-13}	9.125×10^{-10}	2.375×10^{-8}	4.764×10^{-7}	1.370×10^{-10}	0.2523
0.500	2.740	4.885	0	7.773×10^{-14}	2.085×10^{-10}	1.123×10^{-8}	4.764×10^{-7}	6.529×10^{-10}	0.5449
0.500	5.820	4.899	0	1.115×10^{-13}	2.657×10^{-10}	1.269×10^{-8}	4.764×10^{-7}	5.094×10^{-10}	0.4817
1.00	5.260	4.850	0	0	6.739×10^{-11}	6.326×10^{-9}	4.764×10^{-7}	2.179×10^{-9}	0.9859
1.00	3.790	4.849	0	0	6.325×10^{-11}	6.127×10^{-9}	4.764×10^{-7}	2.326×10^{-9}	1.018
5.00	6.640	5.386	0	0	3.326×10^{-12}	1.351×10^{-9}	4.764×10^{-7}	6.080×10^{-8}	4.997
5.00	7.370	5.385	0	0	3.326×10^{-12}	1.351×10^{-9}	4.764×10^{-7}	6.079×10^{-8}	4.997
10.00	8.280	7.349	0	0	9.766×10^{-13}	7.125×10^{-10}	4.764×10^{-7}	2.578×10^{-7}	9.996
10.00	2.970	7.350	0	0	9.762×10^{-13}	7.123×10^{-10}	4.764×10^{-7}	2.579×10^{-7}	9.998

Table A-76: Experimental and predicted concentrations for the solubility of $ThF_4\cdot NH_4F$(cr) at 25°C in NH_4F solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-4b.

Experimental concentrations (m)		Predicted concentrations (m)							
$NH_4F\times10$	$Th_{total}\times10^7$	$Th_{total}\times10^7$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	ThF_2^{6-}	$F^-\times10$
0.5000	0.4570	0.6007	0	0	0	1.208×10^{-12}	3.355×10^{-9}	5.671×10^{-8}	0.5000
0.5000	0.4400	0.6007	0	0	0	1.208×10^{-12}	3.355×10^{-9}	5.671×10^{-8}	0.5000
1.000	0.2800	0.7412	0	0	0	1.863×10^{-13}	9.301×10^{-10}	7.319×10^{-8}	1.000
1.000	0.3190	0.7412	0	0	0	1.863×10^{-13}	9.301×10^{-10}	7.319×10^{-8}	1.000
2.000	0.3710	1.009	0	0	0	0	2.598×10^{-10}	1.006×10^{-7}	2.000
2.000	0.6640	1.009	0	0	0	0	2.598×10^{-10}	1.006×10^{-7}	2.000
5.000	2.440	1.764	0	0	0	0	4.760×10^{-11}	1.764×10^{-7}	5.000
5.000	2.410	1.764	0	0	0	0	4.760×10^{-11}	1.764×10^{-7}	5.000
10.000	15.60	3.253	0	0	0	0	1.269×10^{-11}	3.253×10^{-7}	10.000
10.000	16.20	3.253	0	0	0	0	1.269×10^{-11}	3.253×10^{-7}	10.000

[1994BAG/FOU]

The solubility of well characterised $Th_3(PO_4)_4$(s) was measured at different concentrations of perchloric acid from 0.01 to 1 M. The temperature was presumably "room-temperature", 20−25°C, but the ionic strength seems to have varied between the different test solutions used. Equilibrium was attained after 8 hours and the solubility remained constant for periods of several weeks. Care was taken to ensure that the solubility was not compromised by the presence of colloids. The authors also checked that the solid phase did not change in contact with the aqueous phase. When analysing the experimental solubility data, Baglan *et al.* [1994BAG/FOU] used auxiliary data for the protonation of phosphate and the hydrolysis of Th(IV) that are in good agreement with those selected in the present review. The authors suggest that the solubility product is $\log_{10} K^{\circ}_{s,0} = -(112 \pm 2.1)$ for the reaction:

$$Th_3(PO_4)_4(s) \rightleftharpoons 3Th^{4+} + 4PO_4^{3-}$$

but the procedure used to obtain the solubility product at zero ionic strength is not clear. The proposed solubility product is much lower than reported in [1956CHU/STE], $\log_{10} K^{\circ}_{s,0} = -(79 \pm 1)$. The total concentration of phosphate is so small both in [1994BAG/FOU] and [1956CHU/STE] that one can neglect the formation of phosphate complexes.

[1994OST/BRU]

Östhols *et al.* [1994OST/BRU] made a systematic solubility study with hydrous thorium oxide in carbonate solution to determine the stoichiometry and equilibrium constants of the thorium complexes with carbonate. The solid phase has been dried at room temperature for one week in a vacuum desiccator and characterised as X-ray amorphous, microcrystalline $ThO_2{\cdot}xH_2O(s)$ with a water content of $x = 2.4$. The solubility has been determined in equilibrium with 0, 10 and 100% $CO_2(g)$ and also in batch experiments where the ratio of carbonate/bicarbonate was varied at constant total concentration of carbonate + bicarbonate ($C_{tot} = 0.1$ M). All experiments were performed at 25°C and constant ionic strength ($I = 0.5$ M, $NaClO_4$ medium). The authors have given detailed information about the experimental procedures and primary data. The equilibrium constants used to calculate the concentration of OH^-, HCO_3^- and CO_3^{2-} from the measured the H^+ concentration were taken from [1992GRE/FUG]. The ion interaction (SIT) coefficients used for ionic strength corrections are the same as or close to those selected in the present review.

Östhols *et al.* have also reanalysed the experimental data in [1987JOA/BIG2]; they point out that the Th(IV) EDTA complex used to evaluate the equilibrium constant for the formation of $Th(CO_3)_5^{6-}$ is $Th(EDTA)(OH)^-$, not Th(EDTA)(aq), but it is not clear from [1994OST/BRU] how they arrived at the recalculated value of $\log_{10} \beta_{105}$; this review has therefore reanalysed the data in [1987JOA/BIG2] as described in the Appendix A entry for that paper.

1. Solubility in carbonate-free solution

From the experimental solubility data in carbonate-free solution at $-\log_{10}[H^+] = 3.3-4.1$, Östhols *et al.* [1994OST/BRU] calculated a solubility constant of $\log_{10} {}^*K_{s,0} = (9.37 \pm 0.13)$ in 0.5 M $NaClO_4$ and $\log_{10} {}^*K^{\circ}_{s,0} = (7.3 \pm 0.3)$ at zero ionic strength.

However, the hydrolysis model with the species $Th(OH)^{3+}$, $Th(OH)_3^+$, $Th(OH)_4(aq)$, $Th_2(OH)_2^{2+}$ and $Th_2(OH)_3^{5+}$, and some of the hydrolysis constants taken from [1976BAE/MES], [1991GRE/LAG2] and converted to I = 0.5 M with the SIT, differ considerably from the selections in the present review. Therefore, the solubility constant is re-evaluated using the hydrolysis constants and SIT coefficients selected by this review. The recalculated value, $\log_{10} {}^*K^{\circ}_{s,0} = (8.0 \pm 0.5)$, is included in the selection of the solubility constant for ThO_2(am, hyd). It is comparable to that derived from a solid phase prepared in the same way by [2002NEC/MUL] and to aged thorium oxyhydroxide precipitates (*cf.* Section VII.4.1.1). Polynuclear hydroxide complexes are minor species in the test solutions of [1994OST/BRU] at $-\log_{10}[H^+] = 3.3-4.1$ (*cf.* Figure VII-14).

2. Solubility under 0.1 and 1.0 bar $CO_2(g)$

The solubility measured by Östhols *et al.* [1994OST/BRU] under $CO_2(g)$ partial pressures of 0.1 bar ($-\log_{10}[H^+] = 4.6-7.4$) and 1.0 bar ($-\log_{10}[H^+] = 4.1-6.3$) has been interpreted by the formation of a single ternary complex, (131) = $Th(OH)_3(CO_3)^-$, according to:

$$ThO_2(\text{am, hyd}) + H^+ + H_2O(l) + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^- \qquad (A.85)$$

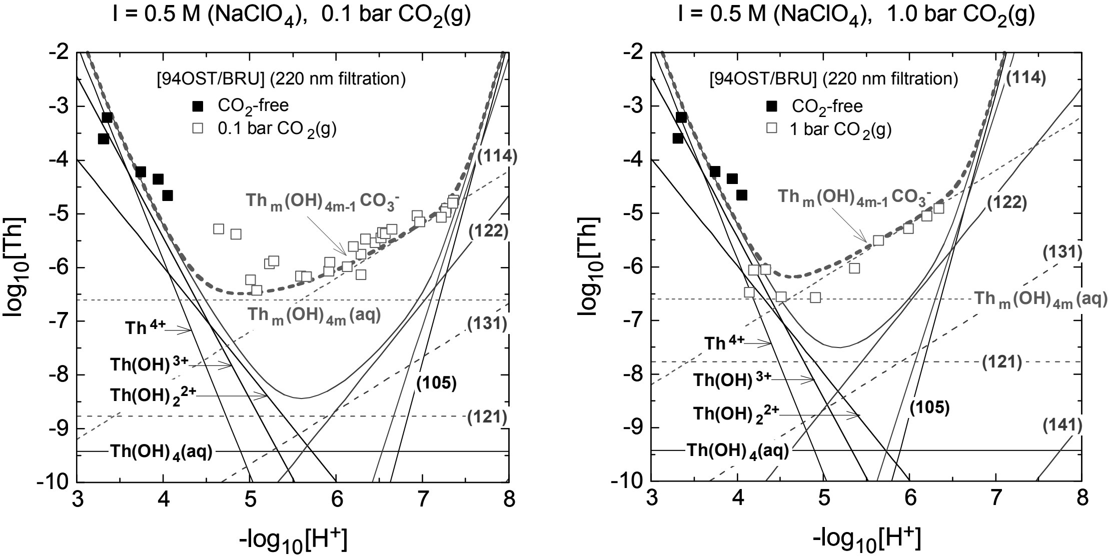
with $\log_{10} {}^*K_{s,(131)}$ (A.85) = (6.1 ± 0.2) at I = 0.5 M, corresponding to $\log_{10} {}^*K^{\circ}_{s,(131)}$ (A.85) = (6.8 ± 0.3) at zero ionic strength [1994OST/BRU]. Combined with the solubility constant of $\log_{10} {}^*K^{\circ}_{s,0} = (8.0 \pm 0.5)$ recalculated by this review from the solubility data in carbonate-free solution, this gives a formation constant of $\log_{10} \beta^{\circ}_{131} = (40.8 \pm 0.3)$ for the reaction:

$$Th^{4+} + 3OH^- + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^- \qquad (A.86)$$

The data have been reanalysed by Altmaier *et al.* [2005ALT/NEC] who identified that the discrepancies between their study and [1994OST/BRU] were due to the presence of colloidal particles (or possibly large polynuclear ternary complexes) that had passed through the filter used by Östhols *et al.* In agreement with the conclusions in [2005NEC/ALT], this review has not accepted the equilibrium constant for the formation of $Th(OH)_3(CO_3)^-$ proposed by Östhols *et al.*

The thorium concentrations measured in the range pH = 4.6−6.5 after 220 nm filtration are comparable to those measured in [2005ALT/NEC] under the same conditions without removing colloidal or polynuclear species. However, [2005ALT/NEC] measured considerably lower thorium concentrations after 1.2 nm ultrafiltration and ultracentrifugation, 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 $Th(OH)_3(CO_3)^-$ but to colloids or large polymers. Thus the thorium concentrations predicted with the equilibrium constants selected by this review (solid lines in Figure A-35) are lower than the experimental data of [1994OST/BRU].

Figure A-35: Solubility of ThO_2(am, hyd) under 0.1 and 1.0 bar CO_2(g) in 0.5 M $NaClO_4$ [1994OST/BRU]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and the solubility constant calculated from the data in carbonate-free solutions, $\log_{10} K^{\circ}_{s,0} = -(48.0 \pm 0.5)$. The dotted curves are calculated with the equilibrium constants proposed by Östhols *et al.* for $Th(OH)_4$(aq) and $Th(OH)_3(CO_3)^-$ (designated here as $Th_m(OH)_{4m}$(aq) and $Th_m(OH)_{4m-1}(CO_3)^-$).



As discussed in Section VII.4.1.2, the concentration of $\log_{10}[Th(OH)_4(aq)] = -6.6$ [1994OST/BRU] is typical for the presence of polynuclear or colloidal species $Th_m(OH)_{4m}$(aq) with $m > 10$. In the presence of carbonate we may additionally assume the formation of carbonate-containing polynuclear species such as $Th_m(OH)_{4m-1}(CO_3)^-$. The solubility data may be described with the reactions:

$$Th(OH)_4(s) \rightleftharpoons (1/m)\ Th_m(OH)_{4m}(aq) \qquad (A.87)$$

and

$$Th_m(OH)_{4m}(aq) + CO_3^{2-} \rightleftharpoons Th_m(OH)_{4m-1}(CO_3)^- + OH^- \qquad (A.88)$$

with $\log_{10} K_{s,(4m,m)}$ (A.87) $= -6.6$ [1994OST/BRU] and $\log_{10} K$ (A.88) $= -1.1$. However, it should be noted that the "equilibrium constants" for Reactions (A.87) and (A.88) are fitting parameters; no equilibrium constants for polynuclear species such as $Th_m(OH)_{4m}$(aq) and $Th_m(OH)_{4m-1}(CO_3)^-$ have been selected by this review.

3. Solubility in carbonate/bicarbonate buffers at C_{tot} = 0.1 M

The analysis of the experimental data in the carbonate/bicarbonate buffers at C_{tot} = 0.1 M and $-\log_{10}[H^+] = 8.2-10.5$ is not affected by the filtration procedure because of the much higher solubility. Based on the knowledge from the previous literature where $\mathrm{Th(CO_3)_5^{6-}}$ has been identified as limiting thorium carbonate complex, Östhols *et al.* interpreted their data with the reaction:

$$\mathrm{ThO_2(am, hyd) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O(l)} \quad (A.89)$$

with

$$\log_{10}[\mathrm{Th(CO_3)_5^{6-}}] - 4\log_{10}[\mathrm{H^+}] = \log_{10}{}^{*}K_{s,(105)} + 5\log_{10}[\mathrm{CO_3^{2-}}] \quad (A.90)$$

and obtained $\log_{10}{}^{*}K_{s,(105)}$ (A.89) = (42.12 ± 0.32) at I = 0.5 M, corresponding to $\log_{10}{}^{*}K^{\circ}_{s,(105)}$ (A.89) = (39.64 ± 0.4) [1994OST/BRU] at zero ionic strength and to $\log_{10}\beta^{\circ}_{105}$ = (31.64 ± 0.64), if combined with the solubility constant of $\log_{10}{}^{*}K^{\circ}_{s,0}$ = (8.0 ± 0.5) recalculated by this review from the solubility data in carbonate-free solution.

The slope of 5 in the plot of $\{\log_{10}[\mathrm{Th(CO_3)_5^{6-}}] - 4\log_{10}[\mathrm{H^+}]\}$ *vs.* $\log_{10}[\mathrm{CO_3^{2-}}]$ (Figure A-36-a) is consistent the presence of $\mathrm{Th(CO_3)_5^{6-}}$ as dominant species. On the other hand, [2005ALT/NEC] claimed that $\mathrm{Th(OH)(CO_3)_4^{5-}}$ is the major complex under these conditions. As shown in Figure A-36-b, the corresponding interpretation of the solubility data in [1994OST/BRU]:

$$\mathrm{ThO_2(am, hyd) + 3H^+ + 4CO_3^{2-} \rightleftharpoons Th(OH)(CO_3)_4^{5-} + H_2O(l)} \quad (A.91)$$

with

$$\log_{10}[\mathrm{Th(OH)(CO_3)_4^{5-}}] - 3\log_{10}[\mathrm{H^+}] = \log_{10}{}^{*}K_{s,(114)} + 4\log_{10}[\mathrm{CO_3^{2-}}] \quad (A.92)$$

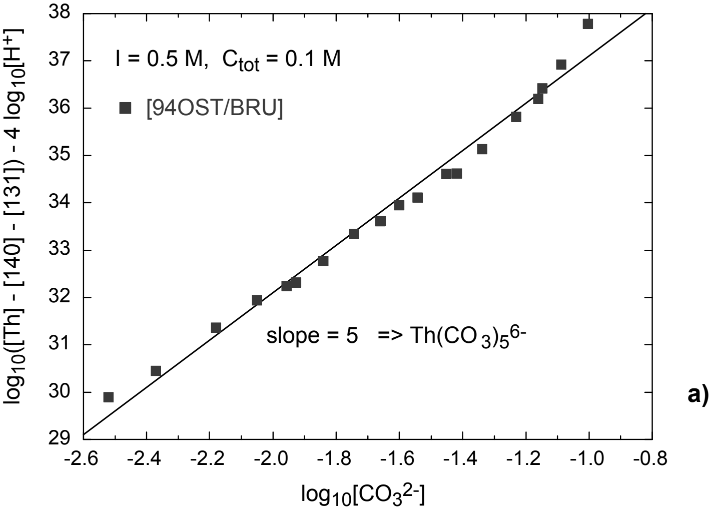
is also consistent with the slope of 4 expected for the plot of $\{\log_{10}[\mathrm{Th(OH)(CO_3)_4^{5-}}] - 3\log_{10}[\mathrm{H^+}]\}$ *vs.* $\log_{10}[\mathrm{CO_3^{2-}}]$.

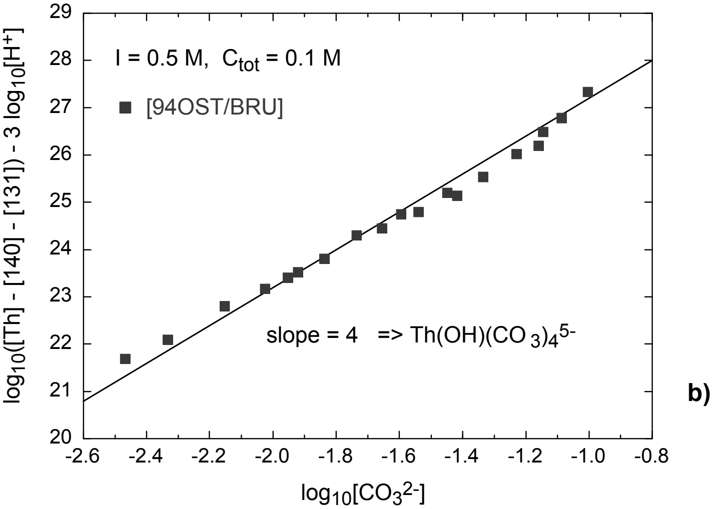
This data set alone does not allow a final conclusion as to the dominant complex under these conditions. Using the additional information from the solubility of $\mathrm{ThO_2}$(am, hyd) under a wider range of experimental conditions at I = 0.5 M [2005ALT/NEC], from an EXAFS spectrum of a saturated solution under very similar conditions at C_{tot} = 0.1 M and $-\log_{10}[\mathrm{H^+}] = -9.16$ in 0.5 M $\mathrm{NaHCO_3}$-$\mathrm{Na_2CO_3}$-NaCl [2006ALT/NEC] and from further EXAFS studies at higher carbonate and bicarbonate concentrations [1997FEL/RAI], [2006ALT/NEC], the present review has selected $\log_{10}\beta^{\circ}_{105}(\mathrm{Th(CO_3)_5^{6-}})$ = (31.0 ± 0.7). This value is somewhat lower than the value of (31.6 ± 0.6) derived above, based on the data interpretation in [1994OST/BRU].

Figure A-36 [1]: Evaluation of the solubility data of [1994OST/BRU] for ThO_2(am, hyd) at I = 0.5 M ($NaHCO_3$-Na_2CO_3-$NaClO_4$) and a total carbonate concentration of C_{tot} = 0.1 M assuming two different dominant reactions:

a) $ThO_2(am, hyd) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O(l)$

b) $ThO_2(am, hyd) + 3H^+ + 4CO_3^{2-} \rightleftharpoons Th(OH)(CO_3)_4^{5-} + H_2O(l)$





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[1] In the plots of Figure A-36 the total thorium concentration in the test solutions is corrected for the contributions from the species $Th(OH)_4$(aq) and $Th(OH)_3(CO_3)^-$ which are, however, very small compared to those of the dominant complexes $Th(CO_3)_5^{6-}$ or $Th(OH)(CO_3)_4^{5-}$.

[1995JOA/BUR]

In this paper, João *et al.* have reinvestigated the Th(IV)-carbonate system using the same experimental method as in their previous study [1987JOA/BIG2]; in addition they have also investigated the Ce(IV)-carbonate system. The experiments were made at three different ionic strengths, 0.025, 0.050 and 0.70 M; there is no information about the temperature and this review has assumed that the experiments refer to "room temperature", (22 ± 2) ºC. In this study the authors have taken the formation of the ternary complex $Th(EDTA)(OH)^-$ into account and have also determined the equilibrium constant, K_{111} for the reaction.

$$Th(EDTA)(aq) + H_2O(l) \rightleftharpoons Th(EDTA)(OH)^- + H^+ \qquad (A.93)$$

The experimental value at ionic strength 0.05, $\log_{10} K_{111} = (7.7 \pm 0.2)$ is in fair agreement with the value reported in [1989SMI/MAR], but the difference between this and the value at ionic strength 0.025, $\log_{10} K_{111} = (9.3 \pm 0.2)$ seems too large for the rather small change in ionic strength. The experimental data refer to a pH slightly below 9, much lower than in [1987JOA/BIG2]. The experimental data are given only in graphs and they are therefore difficult to evaluate. The free carbonate concentration range is very small (between *ca.* 8 and 10 mM), so there could be significant errors in the slope analysis used in [1995JOA/BUR]. The equilibrium constants for the reaction

$$Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} \qquad (A.94)$$

$\log_{10} \beta_5 = 22.0$, 21.6 and 21.4, at ionic strengths 0.025, 0.050 and 0.70 M, respectively, reported in [1995JOA/BUR] are much smaller than that reported in [1987JOA/BIG2] and also those selected in this review. The reason for this seems to be an error in the equation (10), p. 178 in [1995JOA/BUR], where the equation:

$$\frac{D^C}{D^Y} = \frac{K_{111}^Y[\text{EDTA}][\text{H}_Y^+]^3}{\beta_5^C[\text{CO}_3^{2-}]^5[\text{H}_C^+]^4}$$

was transformed into

$$\frac{D^C}{D^Y} = \frac{K_{111}^Y[\text{EDTA}]}{\beta_5^C[\text{CO}_3^{2-}]^5} \times 10^3(10\text{pH}_C - \text{pH}_Y)\,.$$

This transformation implies the simple mathematical error that

$$[\text{H}_Y^+]^3/[\text{H}_C^+]^4 = 10^4\text{pH}_C - 10^3\text{pH}_Y = 10^3(10\text{pH}_C - \text{pH}_Y)$$

instead of the correct $10^{(4\text{pH}_C)}/10^{(3\text{pH}_Y)} = 10^{(4\text{pH}_C - 3\text{pH}_Y)}$. For this reason the equilibrium constants have not been accepted by this review. It is also notable that the Ce(IV) system is claimed to form the complex $Ce(CO_3)_2(aq)$ in the same concentration range where $Th(CO_3)_5^{6-}$ is assumed to be predominant. Ce(IV) forms much stronger hydroxide complexes than Th(IV) and presumably also stronger carbonate complexes. One can therefore not rule out the formation of ternary Ce(IV)-hydroxide-carbonate complexes.

The following experimental observations indicate that the data might be affected by systematic errors:

- The ionic strength dependence of Reaction (A.94) is very large; the values of $\log_{10} K$ at $I = 0.025$, 0.050 and 0.70 are: −9.3, −7.7 and −7.0, respectively; this is not what one expects from the SIT model where the ionic strength effect in this case is determined mainly by the Debye-Hückel term.
- The equilibrium constant for the formation of the assumed complex $\mathrm{Th(CO_3)_5^{6-}}$ differs considerably from that obtained in the previous study [1987JOA/BIG2] using the same experimental method (after the correction discussed above). The equilibrium constant also differs significantly from the values reported in [1994OST/BRU] and [1997FEL/RAI]. There are large similarities in chemical properties of the different actinide(IV) ions and one therefore expects similar equilibrium constants for the complexes formed. This is not the case for the value reported in [1995JOA/BUR].
- It is very surprising to find that the Ce(IV) carbonate system is so different from Th(IV) system. Ce(IV) is much more strongly hydrolysed and under the conditions of the experiment one would expect the formation of ternary hydroxide-carbonate complexes. The formation of $\mathrm{Ce(CO_3)_2(aq)}$ does in the opinion of this review not make chemical sense.
- Using the experimental data in [2005ALT/NEC] and a comparison of with the corresponding U(IV) carbonate system it seems unlikely that the complex $\mathrm{Th(CO_3)_5^{6-}}$ is predominant in the range $-2.05 < \log_{10}[\mathrm{CO_3^{2-}}] < -0.30$.

For these reasons this review has not accepted the equilibrium constants proposed in [1995JOA/BUR].

[1995OST]

The solubility of microcrystalline $\mathrm{ThO_2}$ was measured in the pH range 5 to 13 in the presence of 0.01 and 0.1 M phosphate and in the range 10.5 to 13 in the absence of phosphate. The ionic medium was 1.00 M $\mathrm{NaClO_4}$ and the batch solubility experiments were made at 25°C. The author noted that the solubility in the pH range 5 to 10, $[\mathrm{Th}]_{\mathrm{tot}} = 10^{-6.4}$ M, was close to that predicted using published hydrolysis constants and solubility products. A small increase in solubility was noticed in the presence of 0.1 M phosphate in the pH range 10.5 to 13. The author has analysed the solid phase after equilibrium in the phosphate test solutions and observed that it contained small amounts of phosphate; however no major transformation to solid thorium phosphate phases had taken place. There is no information on equilibrium constants for phosphate complexes in this study, but the author observes that the phosphate complexes cannot compete with the stronger hydroxide complexes under the experimental conditions used. He also suggests that the influence of phosphate on the solubility of Th(IV) in most natural water systems will not be significant; the present review accepts these conclusions.

[1995RAI/FEL]

Rai *et al.* [1995RAI/FEL] measured the solubility of ThO_2(am, hyd) and UO_2(am, hyd) at room temperature (*ca.* 22°C) in $NaHCO_3$ and Na_2CO_3-NaOH or K_2CO_3-NaOH solutions of various carbonate and hydroxide concentrations.

Thorium test solutions:

a. 0.005 − 1.0 M $NaHCO_3$

b. 0.1 − 2.0 M Na_2CO_3

c. 0.001 − 2.0 M Na_2CO_3 containing 0.1 NaOH

d. 1.0 M Na_2CO_3 containing 0.01 − 0.5 M NaOH

Uranium test solutions:

a. 0.02 − 1.0 M $NaHCO_3$ and 0.1 − 2.0 M Na_2CO_3

b. 0.0003 − 2.0 M Na_2CO_3 containing 0.01 NaOH

c. 0.0003 − 2.0 M Na_2CO_3 containing 0.01 NaOH

d. 2.7 M K_2CO_3 containing 0.01 − 0.1 M NaOH

The results show the expected tendency that the solubility of ThO_2(am, hyd) is considerably greater than that of UO_2(am, hyd) at comparable conditions. This paper does not contain a quantitative interpretation but only reports the following qualitative conclusions: The pentacarbonate complex $An(CO_3)_5^{6-}$ is expected to be dominant at high carbonate concentrations while the variation of the solubility with the NaOH concentration (at fixed total carbonate concentration) indicates the formation of ternary complexes like $An(OH)_4(CO_3)^{2-}$ or $An(OH)_3(CO_3)^{-}$. Quantitative models for the solubility of Th(IV) and U(IV) in carbonate solution are reported in the later papers [1997FEL/RAI] and [1998RAI/FEL], respectively. The evaluation of the solubility data for ThO_2(am, hyd) is discussed in detail in the Appendix A entry for [1997FEL/RAI].

[1996BEN/BRA]

Synthesis of $Th_4(PO_4)_4P_2O_7$ was achieved only with a controlled thorium to phosphorus ratio of 2/3 in the starting materials. Mixtures of $Th_4P_6O_{23}$ and ThO_2 were observed at thorium to phosphorus ratios of > 2/3 and of $Th_4P_6O_{23}$ and ThP_2O_7 for ratios of < 2/3. The compound was characterised by powder and single crystal X-ray diffraction, chemical analyses, and infrared spectroscopy. No thermodynamic data were reported.

[1996BOI/COL]

The exploding wire technique was used to measure some physical properties of Th(cr) and Th(l) up to the vicinity of the thorium boiling point (*ca.* 5000 K). The main details of the paper concern the volume expansion and electrical resistivity, which are reported as a function of enthalpy, since no temperatures were measured. This restricts their usefulness for current purposes, since the enthalpy of thorium is not known above 3400 K. However, the results did show relatively distinct breaks at the α to β and melting transformations, from which the authors deduced transition enthalpies of 3.5 and 13.9 $\mathrm{kJ \cdot mol^{-1}}$, in excellent agreement with existing data.

[1996KON]

The infrared spectrum of ThF_4(g) heated to 1300 to 1370 K was recorded with a resolution of 0.5 $\mathrm{cm^{-1}}$ using an optical gas cell with silicon windows. The ν_4 fundamental was found at 116 $\mathrm{cm^{-1}}$ in a low intensity band. This is close to the value of 114 $\mathrm{cm^{-1}}$ for UF_4(g) found earlier by the same team.

[1996RON/HIE]

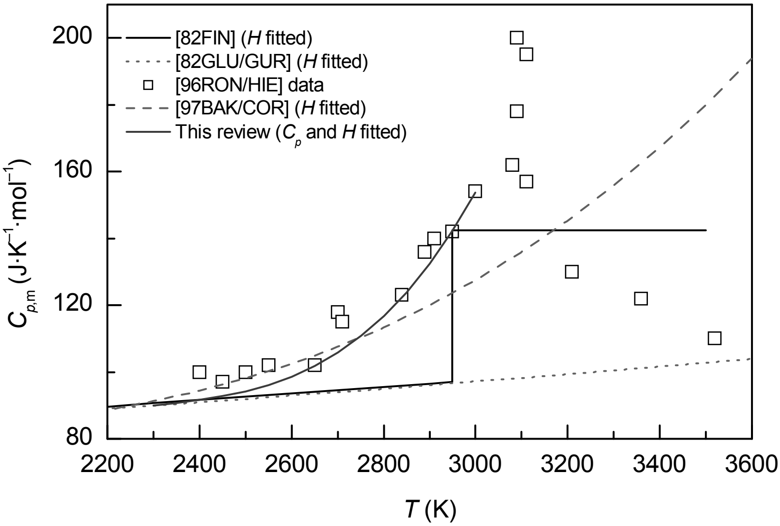
This paper describes a study of some thermophysical properties of ThO_2(cr) at temperatures of 2500 to 4000 K. Small spheres (*ca.* 1 mm diameter) of ThO_2 (99.9% pure) were pulse heated in an autoclave filled with different gases by four symmetrically oriented Nd-YAG laser beams of equal intensity. This heated a shell of the sphere approximately 0.3 mm thickness to temperatures above the melting point and the sample cooling curve was then recorded by a fast multichannel pyrometer. The heat capacity was obtained from the sample cooling rate and any thermodynamic phase transitions occurring were identified from the analysis of the corresponding thermal arrest traces on the cooling curves.

The melting point of essentially stoichiometric thoria was shown to be (3651 ± 17) K, with a pre-melting transition at (3091 ± 6) K. These temperatures are weakly influenced by chemical reduction of the sample. While virtually stoichiometric thoria melts congruently, in the hypostoichiometric oxide the liquidus and solidus temperatures could be clearly observed at O/Th = 1.98.

Ronchi and Hiernaut found that the heat capacity in the region of the pre-melting shows a typical, but broad λ peak, rising from *ca.* 110 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 2400 K to a peak of over 200 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at (3090 ± 10) K, falling again to *ca.* 115 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 3450 K as shown in Figure A-37. The data suggest that these features can be described by a defect model, where cooperative effects lead to a critical order-disorder transition in the oxygen sublattice. A similar second-order transition occurs in a number of compounds with the fluorite structure.

However, the noticeable decrease in the heat capacity above 3100 K is not consistent with the more accurate enthalpy data of Fisher *et al.* [1981FIS/FIN] who made measurements up to 3400 K, and derived an essentially linear $C_{p,\mathrm{m}}$ of 142.3 J·K^{-1}·mol^{-1} from 2950 to 3400 K. The reason for this discrepancy is not clear and further work is required to establish which of these interpretations is correct. But for the purposes of this review, data for $C_{p,\mathrm{m}}$(ThO$_2$,cr) is only required up to 3000 K, in order to process the vapour pressure data, and we have restricted our treatment of the high temperature enthalpy and heat capacity data to this temperature, where the inconsistency is acceptable.

Figure A-37: Fit to C_p and $H(T)-H(298.15\ \mathrm{K})$ for ThO$_2$(cr) from 2300 to 3000 K – Heat capacity.



For this, we have made a simultaneous fit of the heat capacity and enthalpy data from 2300 to 3000 K for $C_{p,\mathrm{m}}$ and $H(T)-H(298.15\ \mathrm{K})$ to a cubic equation (for $C_{p,\mathrm{m}}$), with the constraints that $C_{p,\mathrm{m}}$(2300 K) and $H(2300\ \mathrm{K})-H(298.15\ \mathrm{K})$ are identical to the values from our selected data below 2300 K (essentially the same as those of [1982GLU/GUR]). The fitting used the 15 $C_{p,\mathrm{m}}$ data points from [1996RON/HIE] and 13 data points for $H(T)-H(298.15\ \mathrm{K})$, 5 from [1961HOC/JOH] and 8 from [1981FIS/FIN].

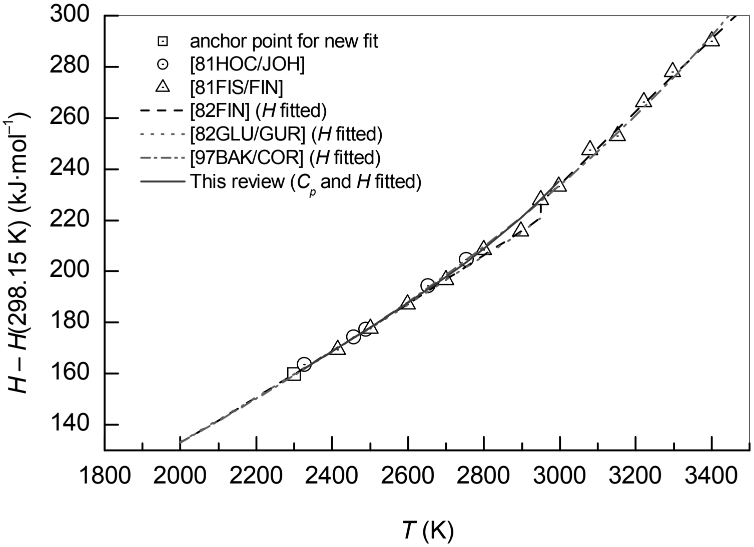
The uncertainty in the measurements of [1981FIS/FIN] is estimated to be at least ±2%, since their calibration differed from a standard sample of NBS molybdenum by 1.5% even at 2500 K, and their errors are likely to increase with temperature. Their reproducibility for duplicate runs was about 0.5%. The uncertainty of the $C_{p,\mathrm{m}}$ measurements by [1996RON/HIE] is much more difficult to estimate, but from their reproducibility (see Figure A-37), we estimate the uncertainty to be at least 6%.

The enthalpy data were therefore given a weighting factor of three in the fitting. The average deviation of the $C_{p,\mathrm{m}}$ data from the fit is $+3.6\%$, with a standard deviation of $\pm3.9\%$, while for the enthalpy data, these values are -0.23% and $\pm0.85\%$, which reflect satisfactorily the relative accuracies of the two data sets.

The resulting fit to the heat capacity is shown in Figure A-37, together with earlier assessments, which have fitted the enthalpy only. The corresponding enthalpy values are shown in Figure A-38 These two figures include the data up to 3500 K, although no data above 3000 K were used in the fitting for this review.

Ronchi and Hiernaut also report the spectral emissivity of the thoria samples, measured during heating up to 4000 K.

Figure A-38: Fit to C_p and $H(T)-H(298.15\text{ K})$ for ThO_2(cr) from 2300 to 3000 K – Enthalpy.



[1997FEL/RAI]

This paper (based on experimental data from [1995RAI/FEL]) is discussed together with [1999FEL/RAI].

The solubility data determined by Rai *et al.* [1995RAI/FEL] in $0.01-0.25$ M $NaHCO_3$, in 1.0 M Na_2CO_3 containing $0.01-0.5$ M NaOH and in $0.001-2.0$ M Na_2CO_3 containing 0.1 NaOH, were used by Felmy *et al.* [1997FEL/RAI] to derive a model for the solubility of ThO_2(am, hyd) in carbonate solution. This model is based on the ion interaction approach of Pitzer [1991PIT] and includes two thorium complexes, the pentacarbonate complex $Th(CO_3)_5^{6-}$ and the ternary complex $Th(OH)_3(CO_3)^-$ proposed by

Östhols *et al.* [1994OST/BRU]. The equilibrium constant $\log_{10}{}^{*}K^{\circ}_{s,(131)}$(A.95) = 6.78 for the reaction:

$$ThO_2(am, hyd) + H^+ + H_2O(l) + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^- \qquad (A.95)$$

was adopted from [1994OST/BRU]; Pitzer parameters for this complex are not reported. The equilibrium constant $\log_{10}{}^{*}K^{\circ}_{s,(105)}$ (A.96) = 37.6 calculated by [1997FEL/RAI] for the reaction:

$$ThO_2(am, hyd) + 4H^+ + 5\,CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O(l) \qquad (A.96)$$

differs by two $\log_{10}$ units from the value of $\log_{10}{}^{*}K^{\circ}_{s,(105)}$ (A.96) = (39.6 ± 0.4) calculated in [1994OST/BRU] with the SIT approach. The binary Pitzer parameters reported by Felmy *et al.* [1997FEL/RAI] for the pair Na^+- $Th(CO_3)_5^{6-}$ ($\beta^{(0)} = 1.31$, $\beta^{(1)} = 30$ kg·mol^{-1}) are reasonable for interactions parameters between ions of these charges. These parameters were applicable to model the solubility of ThO_2(am, hyd) in the investigated $NaHCO_3$ and Na_2CO_3-NaOH solutions [1995RAI/FEL] within an uncertainty range of ± 0.5 $\log_{10}$-units. However, the modelling of the solubility data determined by Östhols *et al.* [1994OST/BRU] at C_{tot} = 0.1 M and I = 0.5 M in $NaClO_4$ media required in addition a mixing parameter with an extremely large value of $\theta(Th(CO_3)_5^{6-} - ClO_4^-) = 5.5$ kg·mol^{-1}.

In a later study Felmy *et al.* [1999FEL/RAI] extended their model to alkaline Na_2CO_3-NaCl solutions. The experimental solubility data determined with ThO_2(am, hyd) in 2.33 and 4.67 m NaCl containing 0.1−2.3 M Na_2CO_3 and 0.1 M NaOH were fitted with mixing parameters of $\theta(Th(CO_3)_5^{6-}\text{-}Cl^-) = 1.8$ kg·mol^{-1} and $\psi(Th(CO_3)_5^{6-}\text{-}Cl^-\text{-}Na^+) = 0.3$ kg^2·mol^{-2}, indicating that the activity coefficients of $Th(CO_3)_5^{6-}$ in Na_2CO_3-NaCl solutions differ considerably from those in Na_2CO_3-$NaClO_4$ solutions.

It should be noted that the model of Felmy *et al.* is neither consistent with the complexes and equilibrium constants selected in the present review nor with the speciation calculated with the SIT approach. Therefore the equilibrium constants selected in the present review must not be used in combination with the Pitzer parameters of Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI].

The predictive capability of the equilibrium constants and SIT coefficients selected in the present review for the ternary Th(IV)-hydroxide-carbonate complexes and $Th(CO_3)_5^{6-}$ is demonstrated in Figure A-39, Figure A-40 and Figure A-41 for the solubility of ThO_2(am, hyd) under the experimental conditions in [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI]. The model calculations are in good agreement with the solubility of ThO_2(am, hyd) at high OH^- and Na_2CO_3 concentrations up to 1.0 M (Figure A-39). At carbonate concentrations above $[CO_3^{2-}]$ = 1.0 M and I > 3 mol·kg^{-1} (Figure A-39), in particular in solutions with additions of NaCl (Figure A-40), the predicted thorium concentrations are up to about 1.5 orders of magnitude lower than the experimental values. As shown by the dashed concentration lines for the species (124) in Figure A-39 and Figure A-40, the solubility at high carbonate concentration and ionic strength can be better described by assuming the formation of the additional ternary complex $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$ with $\log_{10} \beta^{\circ}_{124}$ = (34.3 ± 0.6) and $\varepsilon(\mathrm{Th(OH)_2(CO_3)_4^{6-}}$, $\mathrm{Na^+}) = -(0.3 \pm 0.2)\ \mathrm{kg{\cdot}mol^{-1}}$ as estimated in [2005ALT/NEC]. However, these conditions are beyond the validity range of the SIT model. Moreover, changing $\varepsilon(\mathrm{Th(OH)(CO_3)_4^{5-}}$, $\mathrm{Na^+})$ or $\varepsilon(\mathrm{Th(CO_3)_5^{6-}}$, $\mathrm{Na^+})$ within their uncertainty ranges would also yield a better fit. Therefore the complex $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$ is not selected by the present review.

Felmy *et al.* [1997FEL/RAI] also present EXAFS measurements of Th(IV) in carbonate solutions. The sample compositions are given as 1.0 M $\mathrm{Na_2CO_3}$ + 0.1 M NaOH and 1.0, 0.5, 0.25, 0.17 and 0.10 $\mathrm{NaHCO_3}$, with thorium concentrations ranging from 8.6 mM to 0.1 mM. The thorium concentration of 0.02 mM in a 0.07 M $\mathrm{NaHCO_3}$ solution was too low for XAS analysis. The composition of the first sample (designated as Th-15) cannot be correct, because the solubility of $\mathrm{ThO_2}$(am, hyd) is below 10^{-5} M under these conditions (*cf.*, Figure A-39). Moreover, in another EXAFS study of this group [1997HES/FEL], which is the basis for the EXAFS data reported in [1997FEL/RAI], the composition of sample Th-15 is reported to be 2.0 M $\mathrm{Na_2CO_3}$ + 0.1 M NaOH. The EXAFS parameters derived from the $\mathrm{NaHCO_3}$ solutions, in particular the coordination numbers $\mathrm{N_O}$, $\mathrm{N_C}$ and $\mathrm{N_{Od}}$, differ somewhat from those reported for the same samples (Th-76, Th-74 and Th-71) in [1997HES/FEL], but this does not affect the general conclusions. In the $\mathrm{Na_2CO_3}$ solution and in 1.0 and 0.5 M $\mathrm{NaHCO_3}$ the complex $\mathrm{Th(CO_3)_5^{6-}}$ is the dominant species ($\mathrm{N_O}$ = (10.5 ± 2.7) at $d_{\mathrm{Th-O}}$ = (2.49 ± 0.02) Å, $\mathrm{N_C}$ = (4.4 ± 1.4) at $d_{\mathrm{Th-C}}$ = (3.00 ± 0.02) Å, and $\mathrm{N_{O_d}}$ = (5.9 ± 1.8) at $d_{\mathrm{Th-O_d}}$ = (4.23 ± 0.02) Å). In the 0.25 and 0.17 M $\mathrm{NaHCO_3}$ solutions the distances $d_{\mathrm{Th-O}}$ = (2.50 ± 0.02) Å, $d_{\mathrm{Th-C}}$ = (2.98 ± 0.02) Å, $d_{\mathrm{Th-O_d}}$ = (4.22 ± 0.02) Å ($\mathrm{O_d}$ represents a distal carbonate oxygen atom), and the coordination number of the first oxygen shell ($\mathrm{N_O}$ = (10 ± 1)) remain approximately constant, while the average number of $\mathrm{CO_3^{2-}}$ ligands ($\mathrm{N_C}$ and $\mathrm{N_{Od}}$) decreases to values between 5 and 4. This is consistent with the formation of $\mathrm{Th(OH)(CO_3)_4^{5-}}$. In the 0.10 M $\mathrm{NaHCO_3}$ solution $d_{\mathrm{Th-O}}$ decreases to (2.46 ± 0.02) Å, $\mathrm{N_O}$ to (8.4 ± 2.4), and the number of $\mathrm{CO_3^{2-}}$ ligands to $\mathrm{N_{Od}}$ = (2.2 ± 0.7) [1997FEL/RAI] (or (3.2 ± 1.5) [1997HES/FEL]), indicating the presence of ternary Th(IV)-hydroxide-carbonates complexes with smaller numbers of carbonate ligands, such as $\mathrm{Th(OH)_3(CO_3)^-}$ or $\mathrm{Th(OH)_2(CO_3)_2^{2-}}$, which must noticeably contribute to the speciation. With regard to the large uncertainties of the coordination numbers determined by EXAFS, these results are fairly consistent with the speciation diagram in Figure A-41 that is calculated with the complexes and equilibrium constants selected by this review.

Figure A-39: Solubility of ThO_2(am, hyd) in 1.0 M Na_2CO_3 containing 0.01−1.0 M NaOH and in 0.001−2.0 M Na_2CO_3 containing 0.1 M NaOH: Experimental data from [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC] and calculations based on the equilibrium constants, SIT coefficients and $\log_{10} K^{\circ}_{s,0}$ (aged ThO_2(am, hyd)) = − 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.

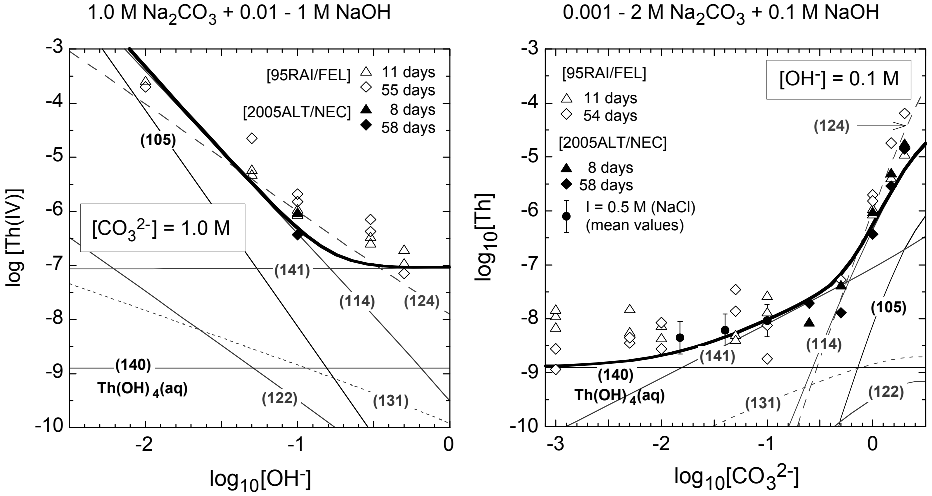


Figure A-40: Solubility of ThO_2(am, hyd) in 2.33 and 4.67 m NaCl containing 0.1 – 2.3 M Na_2CO_3 and 0.1 M NaOH [1999FEL/RAI]. The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{\circ}_{s,0}$ (aged ThO_2(am, hyd)) = – 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.

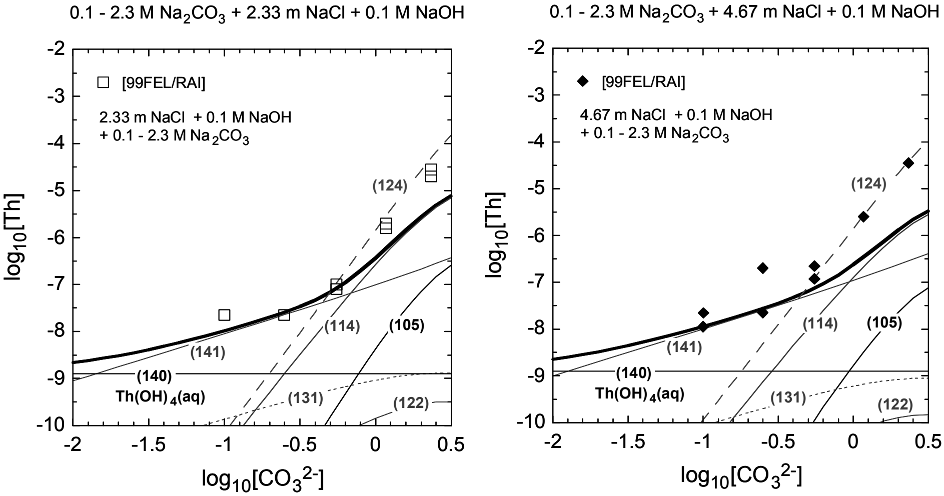
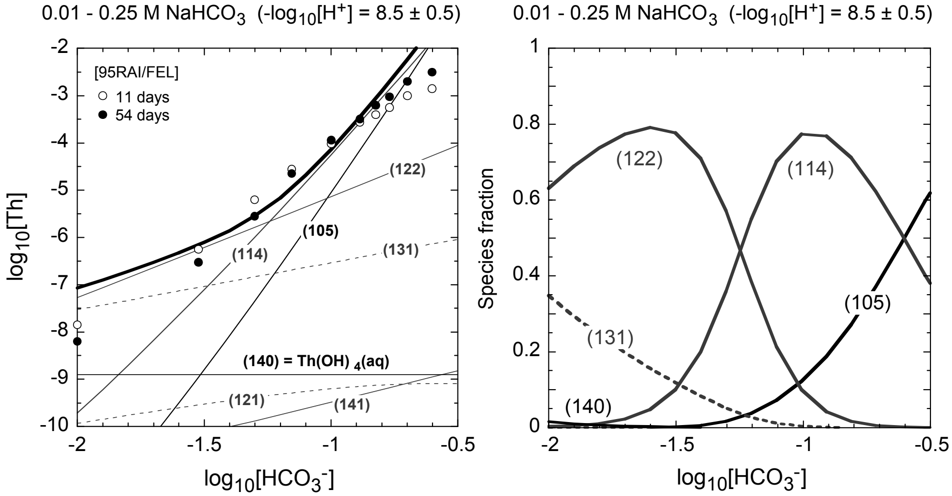


Figure A-41: Solubility of ThO_2(am, hyd) and speciation in 0.01 − 0.25 M $NaHCO_3$ [1995RAI/FEL], [1997FEL/RAI]. The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{\circ}_{s,0}$ (aged ThO_2(am, hyd)) = – 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.



[1997HES/FEL]

In this conference proceedings paper Hess *et al.* [1997HES/FEL] present an EXAFS study of Th(IV) solutions in sodium carbonate and bicarbonate solutions. In three samples, with the solution compositions given as 2 M Na_2CO_3 containing 0.1, 0.5 and 1.0 M NaOH and 1.0 mM Th, the pentacarbonate complex $Th(CO_3)_5^{6-}$ has been identified from the coordination numbers of the first and distal oxygen shells: N_O = (10 ± 1) ($d_{Th–O}$ = (2.49 ± 0.02) Å, $d_{Th–C}$ = (2.99 ± 0.02) Å) and N_{Od} = 5($d_{Th–Od}$ = (4.26 ± 0.02) Å). The fitted number of second shell carbon atoms appears to be too small (N_C = 3.1 − 3.4 at a distance of $d_{Th–C}$ = (3.00 ± 0.02) Å). However, the reported sample compositions cannot be correct, because in these highly alkaline solutions the solubility of ThO_2(am, hyd) is below 10^{-5} M (*cf.* Figure 4 in [1995RAI/FEL] and Figure 1 in [1997FEL/RAI]), much too low for EXAFS analysis.

In the 0.25 and 0.1 M $NaHCO_3$ solutions (pH 9.3 − 9.4) containing 7 mM and 0.1 mM Th, respectively, the distance $d_{Th–O}$ and N_O are approximately the same, but the number of CO_3^{2-} ligands decreases to about (3 ± 1) and the authors postulate the formation of a ternary complex $ThO_{2-x}(CO_3)_3(OH)_x^{(6-x)-}$. However the coordination numbers have large uncertainties and a clear-cut identification of the ternary complexes is not possible.

[1997HOV]

As noted in Appendix A of [2003GUI/FAN], this is an important study as it is a precise determination of the partial molar heat capacity and volume of a M^{4+} ion. By selecting Th(IV) the author has been able to minimise the experimental difficulties due to hydrolysis. The procedure, the data (10 to 55°C) and the data treatment are detailed in the paper. The consistency of the results for the system $Th(ClO_4)_4$ + $HClO_4$ has been tested using Young's rule and the Pitzer ion-interaction model with concordant result over the entire concentration range 1.0 to 2.9 m investigated. Hovey reports $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}$, 298.15 K$) = -(224 \pm 5)$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

In his calculations, the author uses a fit of the existing literature data for the partial molar quantities of $HClO_4$. These calculations are compatible with a value of $C^{\circ}_{p,\mathrm{m}}(\mathrm{ClO_4^-}) = -(25.45 \pm 0.60)$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The author has also reviewed the previous attempts by [1976MOR/MCC] and [1975APE/SAH] to estimate the partial molar heat capacity of Th^{4+} and finds that the results deviate strongly from his own experimental data. The data of Morss and MacCue [1976MOR/MCC] based on integral enthalpies of dilution of $Th(NO_3)_4{\cdot}5H_2O(cr)$ in 0.01 M $HClO_4$ at 15, 25 and 35°C, recalculated using a new value of the partial molar heat capacity of NO_3^-, $C^{\circ}_{p,\mathrm{m}} = -72$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1988HOV/HEP], gives $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}$, 298.15 K$) = -(60 \pm 11)$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, close to the value selected by [1992GRE/FUG] for U^{4+}, $[C^{\circ}_{p,\mathrm{m}}]^{473\mathrm{K}}_{298\mathrm{K}}(\mathrm{U}^{4+}) = -(48 \pm 15)$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The data of Apelbat and Sahar [1975APE/SAH] at 30°C based on measurement of bulk heat capacity of $Th(NO_3)_4$ solutions, given as a linear function of $m^{1/2}$ for the range 0 to 2.9 m, lead to $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}$, 303.15 K$) = 111$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, as calculated by Hovey using $C^{\circ}_{p,\mathrm{m}}(\mathrm{NO_3^-}) = -63.7$ $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ from [1989HOV/HEP]. Hovey plausibly argues that the discrepancy is not surprising, given the fact that specific molalities and heat capacities are not reported and also the improbability of a simple linear equation being able to represent heat capacities over such a wide range of temperature. Hovey [1997HOV] gives additional important data on the variations of $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+})$ with the temperature and on the structure of the Th^{4+} aqueous ion.

The experimental conditions chosen by Hovey, which lead to little hydrolysis and no complexation, are preferable to those of [1976MOR/MCC].

A related paper, [1986HOV/TRE] refers to $C^{\circ}_{p,\mathrm{m}}(\mathrm{Al}^{3+})$, where $C^{\circ}_{p,\mathrm{m}}(\mathrm{Al}^{3+})$ was found to be -119 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, while the Criss-Cobble equation, [1964CRI/COB2] leads to 16 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

It seems that the Criss-Cobble equation for heat capacity from entropy breaks down for highly charged ions. As Hovey noticed, the correspondence between the result of Morss and McCue for Th^{4+} and the Criss-Cobble prediction for U^{4+} could be fortuitous.

[1997KLA/SCH]

These authors claimed the first experimental evidence for the formation of the Th^{3+} ion in aqueous solution, as a result of the reduction of Th^{4+} by hydrazoic acid. The solution was prepared by mixing 7.38 mmol of $ThCl_4$ in 10 mL water with 15mL of a 2.0 M HN_3 solution under nitrogen. An amber solution was obtained immediately and gaseous evolution was observed.

The process was ascribed to the reaction

$$Th^{4+} + HN_3(aq) \rightarrow Th^{3+} + 1.5N_2(g) + H^+ \quad (A.97)$$

based on a value of −3.54 V for the potential corresponding to the reaction

$$1.5N_2(g) + H^+ + e^- \rightarrow HN_3(aq) \quad (A.98)$$

at pH 3.5 and 298.15 K (calculated from the data in [1982WAG/EVA]) and on an estimated value [1986BRA/LAG] of −3.0 V for the Th^{4+}/Th^{3+} standard potential.

However, the experimental observations indicate a rapid reaction and this is contrary to what one would expect for the redox reaction (A.98) that involves $N_2(g)$. The $N_2(g)/HN_3(aq)$ couple is strongly irreversible, as indicated by the stability of HN_3 in dilute aqueous solution, hence the proposed reduction of Th^{4+} would not be thermodynamically controlled as suggested in [1997KLA/SCH].

The Th^{3+} solution was reported to be stable for more than one hour; after that time, slow oxidation by water was reported, with the formation of a white gel-like precipitate assumed to be "thorium oxide hydroxide".

The absorption spectrum (UV-visible, 180−1300 nm) of the solution was characterised by a broad band below 650 nm with a maximum at 460 nm, followed at lower wavelengths by a very intense band with maxima at *ca.* 332 (shoulder), 190, and 185 nm. These features were assigned to $f \rightarrow d$ and metal → ligand allowed transitions. The ESR spectrum of a frozen solution showed a very broad signal with a main g value of 2.19 that the authors indicated to be similar to other f^1 systems.

The conclusions of [1997KLA/SCH] regarding the formation of the Th^{3+} in their experiments were seriously questioned by Ionova *et al.* [1998ION/MAD] (see Appendix A).

[1997RAI/FEL]

This paper is discussed together with [1991FEL/RAI].

[1997SOU/KUS]

Souter *et al.* [1997SOU/KUS] have identified the four gaseous thorium hydride species ThH_n (n = 1 to 4) by examining the IR spectra of the products condensed from the reaction of laser-ablated thorium with $H_2(g)$ in solid argon matrices. In some experiments, a discharge was passed through the Ar-$H_2(g)$ mixture, using a low-power microwave source, to provide a source of H atoms. After deposition, the samples were annealed at 20−40 K. Isotopic substitution with deuterium confirmed the spectral assignments. Estimates of the vibration frequencies by DFT calculations, including quasi-relativistic effects, gave good theoretical support for the assignments and provided additional data on the structures of the hydride molecules.

The resultant structures and vibration frequencies assigned are summarised in Table A-77.

It will be seen from Table A-77, that [1997SOU/KUS] unfortunately only give the calculated vibration frequencies for the IR active modes, so no complete calculation of the thermodynamic properties of the higher hydrides is possible.

Table A-77: Properties of gaseous thorium hydride molecules.

Species	Symmetry and multiplicity of ground state	*r*(Th–H) (Å)	H–Th angle °	Vibration frequencies (cm^{-1})	
				Experimental	DFT calculation
ThH(g)	C∞, doublet	1.985	180	1485.2	1496
ThH_2(g)	C_{2v}, triplet	2.040	114	$\upsilon_1 = 1480.1$	$\upsilon_1 = 1454$
				$\upsilon_3 = 1455.6$	$\upsilon_3 = 1399$
ThH_3(g)	C_{3v}, doublet	2.047	114	$\upsilon_1 = 1435$	$\upsilon_1 = 1475$
					$\upsilon_3 = 1409$
ThH_4(g)	$T_{d,}$, singlet	2.058	109.5	$\upsilon_1 = 1444$	$\upsilon_1 = 1504$
					$\upsilon_3 = 1413$

[1997STE/FEL]

This is one of a series of documents from Felmy and co-workers that use of Gibbs energy minimisation approach combined with nonlinear parameter optimisation to analyse a variety of experimental data to simultaneously solve chemical equilibria involving large number of components and associated species. This particular publication describes a model that allows parameter evaluation for both Pitzer and ESP[1] electrolyte models. A reader interested in these codes should also see [1989FEL/RAI] and [1995FEL]. The fitting code (NONLINT), described in these publications, was upgraded by Felmy[2], to include the capability for simultaneously evaluating SIT parameters and fitting chemical potentials of different chemical species from a variety of experimental data. This modified code is referred to as the “NONLINT-SIT code”. The types of data that can be evaluated using the “NONLINT-SIT code” include: solvent extraction, solubility, ion-exchange, potentiometric, and solid solution.

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[1] Environmental Simulation Program

[2] A. R. Felmy, personal communication, Pacific Northwest National Laboratory, September 2004

[1998BRA/DAC]

The paper presents several different methods of preparing $Th_4(PO_4)_4P_2O_7$, but no thermodynamic data are reported.

[1998ION/MAD]

This paper is a well-documented criticism of the claim of [1997KLA/SCH] (see Appendix A) of the first observation of a Th^{3+} ion in aqueous solution from the reaction

$$Th^{4+} + HN_3(aq) \rightarrow Th^{3+} + 1.5N_2(g) + H^+ \qquad (A.99)$$

in a slightly acidic solution ($pH \approx 3.5$).

The authors questioned the value of E^o (Th^{4+}/Th^{3+}), −3.0 V, chosen by [1997KLA/SCH] from the estimation of [1986BRA/LAG] based on an ionic model which took account the stabilisation of *d* electrons by crystal field effects. A re-evaluation of the crystal field stabilisation effects by [1998ION/MAD] led these authors to propose −3.82 V and −3.35 V as limiting values for this potential, consistent with the earlier estimate −3.7 V by [1973NUG/BAY].

Moreover, [1998ION/MAD] recommended the value of −2.80 V for the standard potential of the reaction

$$1.5N_2(g) + H^+ + e^- \rightarrow HN_3(aq) \qquad (A.100)$$

as listed by Jones [1973JON], instead of that of −3.54 V used by [1997KLA/SCH].

With the potential values adopted by [1998ION/MAD], the reduction of Th^{4+} by hydrazoic acid according to Reaction (A.99) would not be thermodynamically feasible. Moreover, as noted in the Appendix A review of [1997KLA/SCH], the redox couple $N_2(g)/HN_3(aq)$ is highly irreversible and dilute aqueous HN_3 is therefore unlikely to act as a fast reducing agent.

The attribution to Th^{3+} species ($f \rightarrow d$ and Th → ligand allowed transitions) of the features in the absorption spectra observed by [1997KLA/SCH] was also criticised by [1998ION/MAD], who showed that these features could be equally well be assigned to a $N_3^- \rightarrow Th^{4+}$ transition and to the $Cl^- \rightarrow Th^{4+}$ charge transfer.

As far as the ESR spectrum reported by [1997KLA/SCH], [1998ION/MAD] suggested that a sensible discussion was not possible without the measurement of the concentration of spins.

[1998KON/HIL]

An analysis of vapour pressure measurements of a number of actinide tetrahalides is used to infer their molecular structure. The results offer no evidence for deviations from tetrahedral symmetry.

For this analysis a set of consistent spectroscopic data and molecular constants for these species is presented based on recent results of IR spectroscopic measurements for $UCl_4(g)$, $UF_4(g)$ and $ThF_4(g)$. For the thorium tetrahalides, these estimates of molecular parameters have been somewhat overtaken by theoretical calculations using density functional theory. These confirm the tetrahedral structure of the species, and on the whole, the current review has preferred these calculated values to the correlative estimates presented in this paper.

[1998WIE/HEL]

Wierczinski *et al.* [1998WIE/HEL] carried out solubility and sorption experiments at 22°C and 55°C in alkaline cement pore waters of pH 13.22 and 12.45 ($I \approx 0.01$ M). The solubility experiments were performed with microcrystalline ThO_2(am, hyd) prepared and dried as described by [1994OST/BRU]. Thorium concentrations were analysed by ICP-MS and pH was measured with a glass electrode calibrated against pH 10 buffer and 0.1 M NaOH, but the phase separation which may be connected with sorption effects is not reported. During short term experiments (5 hours to 5 days) the authors measured thorium concentrations in the range of 4×10^{-9} to 5×10^{-7} M, while those measured after 11 − 25 days were in the range of 10^{-10} to 10^{-9} M. The mean values of $\log_{10}[\mathrm{Th}]$ calculated from the data given in Table 5 of [1998WIE/HEL] are $-(9.6 \pm 0.4)$ at 22°C and $-(10.0 \pm 0.1)$ at 55°C. These concentrations are comparable with those measured by Jernström *et al.* [2002JER/VUO] ($\log_{10}[\mathrm{Th}] = -(9.5 \pm 1.2)$ at pH 7 − 13 and 22°C) with a ThO_2(am, hyd) solid prepared in the same way.

[1999BHA/MIS]

The authors measured the equilibrium constant of the reaction:

$$\mathrm{BaThO_3(cr) + H_2O(g) \rightleftharpoons ThO_2(cr) + Ba(OH)_2(g)} \qquad \text{(A.101)}$$

from 1548 to 1683 K by the transpiration method. The $BaThO_3$ solid was prepared by heating the nitrates of barium and thorium with citric acid, which acts as an ignition agent. X-ray diffraction showed only the presence of a cubic (actually pseudo-cubic) phase with a = 4.499 Å; no other analysis is given. There was no measurable mass loss when the material was heated *in vacuo* to 1750 K, but there was a measurable loss when heated in $H_2O(g)$. The mass loss at 1643 K as a function of the partial pressure of water was closely proportional to $p_{\mathrm{H_2O}}$, indicating the reaction was that given by the above equation. X-ray diffraction on partially evaporated samples showed them to be a mixture of $BaThO_3(cr)$ and $ThO_2(cr)$ as anticipated. The calculated equilibrium constants from 15 experimental points are well represented by the equation $\ln K = -20306/T + 5.37$. Thus the Gibbs energy of the above reaction is $\Delta_{\mathrm{r}}G_{\mathrm{m}}$ ((A.101), T) = 168834 − 44.648 T ($\mathrm{J\cdot mol^{-1}}$). However, the Gibbs energy of formation of $Ba(OH)_2(g)$ is rather uncertain −Gurvich *et al.* [1994GUR/VEY] report derived enthalpies of formation which vary by more than 60 $\mathrm{kJ\cdot mol^{-1}}$, finally associating an uncertainty of ± 20 $\mathrm{kJ\cdot mol^{-1}}$ with their selected value. However, Ali (Basu) *et al.* [2001ALI/MIS2] have recently measured the pressures of $Ba(OH)_2(g)$ in the reaction $BaO(cr) + H_2O(g) \rightleftharpoons Ba(OH)_2(g)$ from 1346 to 1451 K in exactly the same apparatus as that used by [1999BHA/MIS], to give for:

$$BaO(cr) + H_2O(g) \rightleftharpoons Ba(OH)_2(g) \qquad (A.102)$$

$$[\Delta_r G_m]_{1346K}^{1451K}\ ((A.102), T) = 139620 - 41.074\ T\ (J\cdot mol^{-1})$$

By using these data, we can derive the Gibbs energy of the formation reaction of $BaThO_3(cr)$ from the component oxides directly, eliminating some of the possible experimental errors as well as uncertainties in the thermal function of $Ba(OH)_2(g)$. Thus we find:

$$BaO(cr) + ThO_2(cr) \rightarrow BaThO_3(cr) \qquad (A.103)$$

$$[\Delta_r G_m]_{1548K}^{1683K}\ ((A.103), T) = -29214 + 3.574\ T\ (J\cdot mol^{-1})$$

Although the authors suggest an uncertainty of only $\pm 3.6\ kJ\cdot mol^{-1}$ for these values, we recall the large scatter in the data for $\Delta_f H_m^\circ$ ($Ba(OH)_2$, g, 298.15 K) and prefer to increase the uncertainty quite substantially to $\pm$ 20 $kJ\cdot mol^{-1}$.

These data for $\Delta_r G_m$ (A.103) are compared with those obtained by Knudsen effusion measurements of the pressure of BaO(g) from the decomposition of $BaThO_3(cr)$ by [1999MIS/ALI] in Section XII.1.1.2.

[1999FEL/RAI]

This paper of Felmy and Rai presents an overview on the application of Pitzer's ion interaction equations for modelling the aqueous thermodynamics of actinides. The section on the modelling of thorium in carbonate solution is discussed together with [1997FEL/RAI] in the Appendix A entry for that paper. The Pitzer parameters for the Th^{4+} ion and Th(IV) sulphate and fluoride complexes are discussed in the corresponding main text sections and in the Appendix A entries for [1991FEL/RAI], [1992FEL/RAI] and [1993FEL/RAI].

[1999FOU/LAG]

Fourest *et al.* have prepared and carefully characterised the solid $Th_4(PO_4)_4\cdot P_2O_7(s)$ and subsequently measured its solubility in the pH range 0 to 10.5; the temperature was 25°C and the ionic medium 0.1 M $NaClO_4$. The authors have used different analytical methods to determine the solubility and the stoichiometry of the solid phases, all of which are described in detail. The experimental solubility curve, Figure 3 in [1999FOU/LAG], has been divided in three linear sections: at pH < 1.5 the slope of $\log_{10} [Th]_{tot}$ *vs.* pH is -1.10, between $1.5 < pH < 5$, the slope is -0.6 and above pH 5 the slope is zero. The division of the solubility curve seems arbitrary to this review, and the solubility might well be a continuous function of pH. To complicate matters the authors note that $Th_4(PO_4)_4\cdot P_2O_7(s)$ is not formed from the over-saturation side and accordingly the system is not in true equilibrium; the diphosphate ion is also not a stable species and will transform to monophosphate species with a rate that depends on pH and temperature. The authors have used experimental data obtained after an equilibration time of one day and assumed that they can be used to describe an "apparent" equilibrium. The authors have considered the possibility of phase transformation of $Th_4(PO_4)_4{\cdot}P_2O_7(s)$ to form $Th(HPO_4)_2(s)$ and $Th(OH)_4(s)$. It is difficult to judge from the information presented if this has taken place, or not (there does not seem to be an analysis of the solid phases at different pH). The present review is not convinced by the analysis made by Fourest *et al.* but a phase transformation seems possible.

[1999KUS/AND]

The paper deals mainly with the vibrational frequencies of NMO molecules which are formed when laser-ablated Zr, Hf, and Th atoms react with NO. However, additional frequencies at 735.0 and 787.3 cm^{-1} for the experiments involving ^{16}O species and Th were attributed to ThO_2 molecules. These values are essentially the same as those observed by Gabelnick *et al.* [1974GAB/REE].

[1999MIS/ALI]

The authors measured the decomposition pressure of $BaThO_3(cr)$ according to the reaction:

$$BaThO_3(cr) \rightleftharpoons ThO_2(cr) + BaO(g) \tag{A.104}$$

from 1770 to 2136 K by weight-loss Knudsen effusion from tungsten cells. The $BaThO_3$ solid was prepared by heating the nitrates of barium and thorium with citric acid, which acts as an ignition agent. The purity, stated to be >99.9% was checked by unspecified chemical analyses and X-ray diffraction. Moisture was removed from the sample before use by heating to 1673 K in flowing argon. X-ray diffraction on partially evaporated samples showed them to be a mixture of $BaThO_3(cr)$ and $ThO_2(cr)$ as anticipated. The thermodynamic data for the Ba−O system indicate that there are negligible amounts of species other than BaO(g) in the vapour under the experimental conditions. The calculated decomposition pressures from 31 experimental points are well represented by the equation $\log_{10} p_{BaO}/\text{bar} = -21943/T + 6.705$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ ((A.104), T) = 420104 − 128.376 T (J·mol^{-1}). The Gibbs energy of the reaction $BaO(cr) \rightleftharpoons BaO(g)$ over the experimental temperature range is given by 398684 – 131.434 T (J·mol^{-1}), where the data are taken from the recent assessment by [1994GUR/VEY]. Their values for BaO(cr) at 298.15 K differ very slightly from those in Table IV-1), but these differences would be reflected in the data for BaO(g) also. The Gibbs energy of the formation reaction of $BaThO_3(cr)$ from the component oxides is thus:

$$[\Delta_r G_m]_{1770\text{K}}^{2136\text{K}} \text{((A.104), } T) = -21420 - 3.058\,T\,(\text{J·mol}^{-1})$$

The small value of the entropy change of this all-solid reaction gives confidence in the experimental results.

[1999MOL/DEN]

The structure of M^{4+} and MF^{3+}, where M = U and Th were determined using L_{III} edge EXAFS in test solutions of 1.5 M $HClO_4$, where the total concentration of Th(IV) was 0.03 and 0.05 M. A standard analysis of the scattering data indicated (10.8 ± 0.5) water molecules in the first coordination sphere of both M^{4+} ions and a Th–O distance of (2.45 ± 0.01) Å. The authors suggest that the most likely coordination number is (10 ± 1) for both ions and this review accepts this estimate as it is in good agreement with previous large angle X-ray scattering data [1968JOH2] and theoretical data [2001YAN/TSU], [2002YAN/TSU]. In the fluoride test solutions the EXAFS data gave Th–F and Th–O distances of (2.14 ± 0.01) Å and (2.48 ± 0.01) Å, respectively; the first sphere coordination number is still (10 ± 1). There are indications of an asymmetric distribution of the Th–O distances as expected for both tricapped trigonal bipyramid and square antiprism geometries.

[2000ALI/MIS]

The authors measured the decomposition pressure of Cs_2ThO_3(cr) according to the reaction:

$$Cs_2ThO_3(cr) \rightleftharpoons ThO_2(cr) + Cs_2O(g) \qquad (A.105)$$

from 1100 to 1254 K by weight-loss Knudsen effusion. The Cs_2ThO_3 solid was prepared by heating caesium iodide and hydrated thorium nitrate with citric acid, which acts as an ignition agent. The purity was checked by unspecified chemical analyses and X-ray diffraction; TGA and DSC were also used. The total carbon content was 0.08 wt%. Moisture was removed from the sample before use by heating to 1250 K in the Knudsen cell. X-ray diffraction on partially evaporated samples showed them to be a mixture of Cs_2ThO_3(cr) and ThO_2(cr) as anticipated, (but no details are given). The thermodynamic data for the Cs-O system indicate that there are quite negligible amounts of species other than Cs_2O(g) in the vapour under the experimental conditions. The initial rate of effusion of Cs-bearing species was high, but fell rapidly and remained constant after a few minutes. This behaviour was attributed to the formation of CsOH(g) from the residual water vapour in the system. The subsequent contribution of CsOH(g) to the pressure was estimated to be less than 1%. The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{Cs_2O}/\text{bar} = -13942/T + 6.939$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ (A.105) = 266916 − 132.842 T ($J \cdot mol^{-1}$). The Gibbs energy of the reaction $Cs_2O(l) \rightleftharpoons Cs_2O(g)$ over the experimental temperature range is given by 152692 − 107.587 T ($J \cdot mol^{-1}$); where the data are taken from the equilibrium constant given in [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of Cs_2ThO_3(cr) from the component oxides is thus:

$$Cs_2O(l) + ThO_2(cr) \rightarrow Cs_2ThO_3(cr) \qquad (A.106)$$

$$[\Delta_r G_m]_{1100\,K}^{1254\,K}((A.106), T) = -114224 + 25.254\,T\ (J \cdot mol^{-1})$$

Since the entropy of fusion of Cs_2O is 26.042 $J{\cdot}mol^{-1}{\cdot}K^{-1}$, the entropy change for the metastable reaction involving $Cs_2O(cr)$ would be close to zero, which gives confidence in the experimental results. Combination of the values in the above equation with the values for $\Delta_f G_m^o$ (Cs_2O, l) [1982GLU/GUR] and $\Delta_f G_m^o$ (ThO_2, l) (this review) gives finally:

$$[\Delta_f G_m]_{1100K}^{1254K} (Cs_2ThO_3, \text{cr}, T) = -1780323 + 441.26\, T\, (J{\cdot}mol^{-1})$$

where the standard state for Cs is Cs(g) in this temperature range. The uncertainty in these values is estimated to be at least 20 $kJ{\cdot}mol^{-1}$, mainly from the uncertainty in $\Delta_f H_m^o$ (Cs_2O, g, 298.15 K) which is given as 15 $kJ{\cdot}mol^{-1}$ by [1982GLU/GUR].

Since there are no other thermodynamic data for $Cs_2ThO_3(cr)$, no further processing of these results is possible, and no values are selected for the review.

[2000BUN/KNO]

This paper is discussed with [2003NEC/ALT].

[2000EKB/ALB]

This is a study of the hydrolysis of Th^{4+} that includes potentiometric titration data and liquid-liquid extraction data of the type previously described in [1992ENG/ALB]. In the latter case the extractant, acetylacetonate, forms both binary complexes ThL_n^{4-n}, and presumably ternary complexes $ThL_n(OH)_m^{4-n-m}$ in the aqueous phase; the possible formation of ternary thorium-acetylacetonate-hydroxide complexes was not considered in [2000EKB/ALB]. The potentiometric experiments have been made at three different temperatures, 15.0, 25.0 and 35.0°C in a 1 M $NaClO_4$ ionic medium; the liquid-liquid extraction experiments have been performed at 25°C. The potentiometric data have been collected using standard methods, with $[Th]_{tot}$ varying between 10^{-5} and 10^{-4} M in the pH range 3.23 − 4.47. The measured pH values have been converted to $-\log_{10}[H^+]$. The authors have used very small concentrations of total thorium and under these conditions the experiments are strongly dependent on the presence of protolytic impurities in the ionic medium, the presence of 10 ppm Fe or Al will result in a concentrations of about 0.02 mM in 1 M $NaClO_4$; impurity levels of this magnitude are common in commercial sodium perchlorate. The Sillén group therefore developed special techniques to prepare $NaClO_4$. The primary experimental data are given in the paper and they have been analysed using the MINIQUAD least-squares program with simultaneous minimisation of $[H_{tot,calc} - H_{tot,exp}]^2$ and $[Th_{tot,calc} - Th_{tot,exp}]^2$; the standard deviation of the fit is given in Table II of [2000EKB/ALB] but is not defined, nor is there a comparison between experimental and calculated values of H_{tot} and Th_{tot} that would allow identification of systematic errors. The equilibrium constants and the estimated uncertainty deduced from potentiometry are given in Table A-78; the uncertainties in the $\log_{10}{}^*\beta_{n,m}$ values are seriously underestimated and should be increased by at least a factor five as judged by this review.

The enthalpy and entropy of reaction have been estimated from $\log_{10}{}^{*}\beta_{n,m}$ at 15, 25 and 35°C assuming $\Delta_r C_{p,\mathrm{m}} = 0$; the uncertainties in these values are also underestimated in the opinion of this review.

Table A-78: Potentiometric equilibrium constants $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$, for thorium hydroxide complexes in 1 M $NaClO_4$.

t (°C)	Total concentrations of Th (mM)	Species (n,m)	$\log_{10}{}^{*}\beta_{n,m}$ (± 1σ)	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})
15	0.0096 – 0.104	(1,1)	– 3.34 ± 0.05		
		(2,1)	– 8.78 ± 0.02		
		(8,4)	– 20.55 ± 0.01		
		(15,6)	– 41.44 ± 0.03		
25	0.0093 – 0.0989	(1,1)	– 3.35 ± 0.06	38 ± 6	60 ± 20
		(2,1)	– 8.55 ± 0.02	36 ± 1	– 44 ± 4
		(8,4)	– 19.18 ± 0.01	191 ± 3	280 ± 10
		(15,6)	– 39.01 ± 0.04	410 ± 60	600 ± 200
25	0.0116 – 0.123	(2,1)	– 8.54 ± 0.02		
		(8,4)	– 18.95 ± 0.01		
		(15,6)	– 40.07 ± 0.04		
35	0.0104 – 0.103	(1,1)	– 3.19 ± 0.07		
		(2,1)	– 8.36 ± 0.04		
		(8,4)	– 17.86 ± 0.01		
		(15,6)	– 36.58 ± 0.04		

In order to determine a precise value of the first mononuclear hydrolysis constant, additional potentiometric measurements were performed at each temperature in the pH range 1.8 − 3.1. Besides a minor contribution from $\mathrm{Th_4(OH)_8^{8+}}$, the mononuclear complex $ThOH^{3+}$ was the only hydroxide complex observed in this pH range. The following equilibrium constants were calculated:

$$\log_{10}{}^{*}\beta_{1,1}\,(1.0\ \mathrm{M\ NaClO_4,}\ 15°\mathrm{C}) = -(3.6 \pm 0.1),$$
$$\log_{10}{}^{*}\beta_{1,1}\,(1.0\ \mathrm{M\ NaClO_4}\ 25°\mathrm{C}) = -(3.3 \pm 0.1),$$
$$\log_{10}{}^{*}\beta_{1,1}\,(1.0\ \mathrm{M\ NaClO_4}\ 35°\mathrm{C}) = -(3.2 \pm 0.1).$$

The liquid-liquid extraction study has been made at $[\mathrm{Th}]_{\mathrm{tot}}$ below 10^{-5} M, typically at 10^{-7} M; under these conditions the formation of polynuclear complexes and colloids should be minimised. The experimental data have been evaluated in the same way as in [1992ENG/ALB] – that is, the formation of ternary complexes has not been considered. The method requires a simultaneous determination of the equilibrium constants for the binary Th(IV)-OH– and Th(IV)-acetylacetonate systems as indicated in Eqs. (1) and (2) of [2000EKB/ALB]. The authors do not report the total concentration of HL (acetylacetone) used and only some of the experimental $\log_{10} D$ – $\log_{10}[\mathrm{H}^+]$ data are given in Table AII of [2000EKB/ALB]). The equilibrium constants for the acetylacetonate complexes differ significantly from those in [1992ENG/ALB] and the reported uncertainty is much smaller. This may not be the result of improved experimental technique, but the use of a smaller range of total concentrations of acetylacetone (but there is no information on this in the paper). The authors have divided the analysis of the extraction data into two parts, where data below pH 8.3 are assumed to be dominated by the formation of acetylacetonato complexes; these data were used to determine the equilibrium constants for ThL_n^{4-n}. The data at higher pH were then used to determine the equilibrium constants for $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)}_4$. This review has objections to this procedure; ternary complexes have not been taken into account and the authors have not considered the possibility of formation of ThL_5^- that also will result in a decrease of $\log_{10}D$. The following speciation diagram (Figure A-42) illustrates these points. The assumption that binary hydroxide complexes are negligible is only justified at $-\log_{10}[\mathrm{H}^+] < 6$ (varies with the total concentration of acetylacetone). The equilibrium constants for the formation of $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)}_4\mathrm{(aq)}$ suggested are $\log_{10} {}^*\beta(\mathrm{Th(OH)}_3^+) = -(14.9 \pm 2.8)$ and $\log_{10} {}^*\beta\ (\mathrm{Th(OH)}_4,\ \mathrm{aq}) = -(22.0 \pm 0.4)$. The equilibrium constants have been determined also at 15 and 35°C.

Figure A-42 illustrates the effect of assuming that, in addition to the complexes ThL_n^{4-n} (with $\log_{10} \beta_{1,n,0}$ = 9.0, 16.7, 22.8 and 27.4 for n = 1−4 and 25°C [2000EKB/ALB]), the negatively charged complexes ThL_5^- (with $\log_{10} \beta_{1,5,0} = 27.4$) and $\mathrm{ThL_4(OH)^-}$ (with $\log_{10} {}^*\beta_{1,4,1} = 16.0$) are formed. These estimated equilibrium constants correspond to the sums of $\log_{10} \beta_{1,4,0}$ and the following stepwise constants for the reactions:

$$\mathrm{ThL_4 + L^- \rightleftharpoons ThL_5^-} \qquad \log_{10}K = 0.6$$

$$\mathrm{ThL_4 + H_2O(l) \rightleftharpoons ThL_4(OH)^- + H^+} \qquad \log_{10}{}^*K = -11.4.$$

It is obvious that these constants have a noticeable effect on the distribution curve at high pH and accordingly on the model used in [2000EKB/ALB].

The overall results proposed by Ekberg *et al.* [2000EKB/ALB] in Table V of their paper, combining both potentiometric and solvent extraction data, are summarised in Table A-79. The equilibrium constant for $\mathrm{Th_4(OH)_8^{8+}}$ at 25°C is in good agreement with the value calculated from potentiometric data of [1954HIE], [1954KRA/HOL], [1965BAE/MEY] in 1.0 M $\mathrm{NaClO_4}$ at 25°C. The equilibrium constant proposed for $\mathrm{Th_6(OH)_{15}^{9+}}$ at 25°C differs considerably and is about 2 $\log_{10}$-units lower. The enthalpies and entropies of reaction differ significantly from those reported in [1965BAE/MEY].

The equilibrium constants for the mononuclear hydroxide complexes, including the values for $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)_4(aq)}$ which are exclusively derived from the solvent extraction study, were found to be consistent with solubility data for $\mathrm{ThO_2}$(am, hyd) [2001NEC/KIM], [2002NEC/MUL]. However, the stoichiometry of the complexes and their equilibrium constants are based on the assumption that the species ThL_5^- and $ThL_4(OH)^-$ are not formed in significant amounts and this has not been verified.

Figure A-42: Speciation diagram for the Th(IV) acetylacetonate system at 25°C, based on the equilibrium constants for ThL_n^{4-n} (n = 1−4) from [2000EKB/ALB] and the values estimated by this review for ThL_5^- and $ThL_4(OH)^-$. The total concentration of L is constant at 0.05 M and that of Th at 10^{-7} M. Note that the binary hydroxide complexes have not been included in this diagram. They start to influence the species distribution around pH 6.

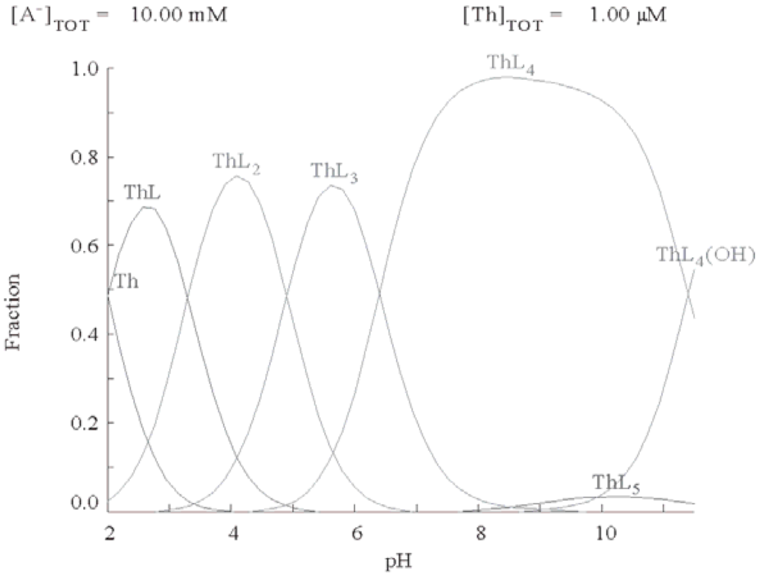


Table A-79: Equilibrium constants, enthalpies and entropies of reaction proposed in [2000EKB/ALB] for the formation of Th(IV) hydroxide complexes in 1.0 M $NaClO_4$.

Complex	$-\log_{10} {}^*\beta_{n,m}$			$\Delta_r H_m$	$\Delta_r S_m$
	15°C	25°C	35°C	(kJ·mol⁻¹)	(J·K⁻¹·mol⁻¹)
$ThOH^{3+}$	3.6 ± 0.1	3.3 ± 0.1	3.2 ± 0.1	38 ± 6	60 ± 20
$Th(OH)_2^{2+}$	8.8 ± 0.1	8.6 ± 0.1	8.4 ± 0.1	36 ± 1	− 44 ± 4
$Th(OH)_3^+$	14.9 ± 2.8	14.2 [a]	12.7 ± 3.5	190 ± 40	300 ± 100
$Th(OH)_4(aq)$	22.0 ± 0.4	19.4 ± 0.5	17.8 ± 0.4	360 ± 40	800 ± 100
$Th_4(OH)_8^{8+}$	20.2 ± 0.3	19.1 ± 0.1	18.0 ± 0.1	191 ± 3	280 ± 10
$Th_6(OH)_{15}^{9+}$	41.4 ± 0.2	39.5 ± 0.2	36.6 ± 0.2	410 ± 60	600 ± 200

a: Estimated from other data for mononuclear hydroxide complexes at 25°C and the values for $Th(OH)_3^+$ at 15°C and 35°C.

[2000FAR/GRE]

This study describes the rate and mechanism of water exchange between $U(H_2O)_{10}^{4+}$, $UF(H_2O)_9^{3+}$, $Th(H_2O)_{10}^{4+}$ and the solvent water as studied by ^{17}O NMR. The rate of exchange is significantly larger for Th^{4+}, $k_{ex} > 5\times10^7\ s^{-1}$ than for the U^{4+}, $k_{ex} = 5.4\times10^6\ s^{-1}$. The mechanism for the exchange depends on the coordination number; for $Th(H_2O)_9^{4+}$ the theoretical data in [2002YAN/TSU] indicate that a dissociative mechanism can be excluded as the energy of the dissociative intermediate is much higher in energy than that for the associative intermediate. On the other hand if Th^{4+} is ten-coordinated, $Th(H_2O)_{10}^{4+}$, the reaction mechanism is most probably dissociative.

[2000FOU/VIN]

Fourest *et al.* [2000FOU/VIN] performed leaching experiments at 25°C and 90°C with ThO_2(cr) powder in pure water and four synthetic granite waters (I = 0.01−0.3 M) at pH 6.6−9.2 and carbonate/bicarbonate concentrations corresponding to carbon dioxide partial pressures of $p_{CO_2} = 10^{-6}$ bar for solutions 1 (final pH = 8.0, 25°C) and 3 (pH = 9.2, 90°C) and 10^{-3} bar for solutions 2 (pH = 6.6, 25°C) and 4 (pH = 7.1, 90°C). The crystalline thorium dioxide was prepared from oxalate calcined up to 1600°C. After 31 days, the thorium concentrations in the batch samples were measured by ICP-MS analysis after centrifugation at 3500 rpm and subsequent ultracentrifugation at 50000 rpm. An effect of carbonate was not observed, which is consistent with the data on Th(IV) carbonate complexes reported by [1994OST/BRU], [1997FEL/RAI] and [2005ALT/NEC].

The mean values of $\log_{10}$[Th] calculated from the data given in Table 4 of [2000FOU/VIN] are −(10.3 ± 0.7) at 25°C and −(8.3 ± 0.4) at 90°C. These values are orders of magnitude higher than expected from $\Delta_f G_m^\circ$ (ThO_2, cr, 298.15 K) = −(1169.0 ± 3.5) kJ·mol^{-1}, corresponding to $\log_{10}{}^{*}K_{s,0}^\circ$ (ThO_2, cr, 298.15 K) = (1.77 ± 1.11), and $\log_{10}{}^{*}\beta_{4,1}^\circ = -(17.4 \pm 0.7)$ selected by this review. These values yield an equilibrium constant of $\log_{10} K_{s,4}^\circ$ (ThO_2, cr) = −(15.6 ± 1.3) for the reaction:

$$ThO_2(cr) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq).$$

The thorium concentrations determined by Fourest *et al.* [2000FOU/VIN] with crystalline thorium dioxide are close to experimental $\log_{10} K_{s,4}$ values for amorphous hydroxides or hydrous oxides ThO_2(am, hyd).

[2000GAG/SKY]

Six different DFT functionals have been used to predict the structure and molecular properties of the four thorium tetrahalides gaseous molecules, giving reasonably consistent values. All the gaseous species are predicted to have tetrahedral symmetry. The calculated interatomic distances agree in general with the experimental electron diffraction results to within 0.05 Å. For the harmonic vibration frequencies, agreement with the four known values (ν_3 and ν_4 for ThF_4 and ν_3 for $ThCl_4$ and $ThBr_4$) is within 15% for all the models. The authors suggest that for thermodynamic calculations, the vibration frequencies from the B3LYP functional should be preferred to empirical estimates.

[2000RAI/MOO]

The solubility of the following thorium oxide phases was studied in 0.1 M NaCl as a function of time and pH (activity scale) at two different temperatures, (23 ± 2) and (90 ± 2)°C: a) an amorphous ThO_2(am, hyd) precipitate purified by washing with water, b) crystalline ThO_2(cr) prepared by heating thorium oxalate at 750°C, and c) a microcrystalline phase obtained by thermal transformation of the amorphous phase at 90°C, designated as $ThO_2(am \rightarrow cr)$. Preparation and characterisation of the solid phases as well as the experimental procedures for measuring the solubility are described in detail, as are the details about the calculations.

The solubility of amorphous ThO_2(am, hyd) was determined from undersaturation at 23°C and pH 4−5 after equilibration of the suspensions for 5−22 days. Analogous experiments were performed with crystalline ThO_2(cr) in the pH range 1.3 to 3.5 at 23°C (equilibration times: 11−794 days) and 90°C (equilibration time: 12 days). At 23°C the solubility of the amorphous phase was greater than 10^{-2} M at pH < 4 while that of the crystalline phase decreased to values below 10^{-9} at pH > 3. The solubility data determined with ThO_2(cr) at 23°C in the pH range 1.3 to 2.0, where hydrolysis is negligible, decreased approximately with the slope of −4 as expected for $\log_{10} [Th^{4+}]$ *vs.* pH. However, the authors were not sure whether equilibrium was reached and considered the measured thorium concentrations as lower limit for the solubility of ThO_2(cr) at 23°C. The thorium concentrations measured at pH 2.0−3.5 after equilibration at 23°C for more than two years were unexpectedly high and independent of pH, indicating that they were not equilibrium values. They decreased to the expected values after storing the samples for two weeks at 90°C and readjusting them for 1 day at 23°C. This observation was ascribed to the crystallinisation of small amorphous fractions of the bulk solid.

A similar observation, the thermal transformation of the initially amorphous ThO_2(am, hyd) precipitate into a microcrystalline solid phase, was made at 90°C and pH 1.5−3.0. The equilibrium between this $ThO_2(am \rightarrow cr)$ phase and Th^{4+} was reached from the direction of oversaturation. The solubility data measured with this $ThO_2(am \rightarrow cr)$ phase after 52−76 days at 90°C show the expected dependence on pH, however, but at a solubility about 2.2 $\log_{10}$-units higher level than the value determined with ThO_2(cr) from undersaturation.

Rai *et al.* have used the Pitzer model to interpret the solubility data and calculate the solubility products for the different thorium oxide phases: $\log_{10} K^{\circ}_{s,0} = -(44.9 \pm 0.5)$ for ThO_2(am) at 23°C, ≥ -56.9 for ThO_2(cr) at 23°C, $-(51.4 \pm 0.2)$ for ThO_2(cr) at 90°C, and $-(49.2 \pm 0.2)$ for $ThO_2(am \rightarrow cr)$ at 90°C. The corresponding interaction parameters are taken from an earlier study [1997RAI/FEL]. However, as shown in Figure VI-5, Section VI.3.2, the activity coefficient calculated with these interaction coefficients for Th^{4+} in 0.1 M NaCl differs by about two orders of magnitude from $\gamma_{Th^{4+}}$ calculated with the SIT and $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$ kg·mol^{-1}. In addition, Rai *et al.* have not taken hydrolysis into account when evaluating the solubility products. Only part of the experimental solubility data have been obtained in a pH range where hydrolysis can be neglected. Therefore this review has used the SIT and the selected data for Th(IV) hydroxide complexes to recalculate the solubility constants from the experimental data in [2000RAI/MOO].

The re-evaluation of the solubility data for fresh ThO_2(am, hyd) at 23°C is shown in Figure A-43. Using the hydrolysis constants and SIT coefficients selected in the present review, the tetranuclear complex $Th_4(OH)_{12}^{4+}$ is found to be the predominant species in saturated solutions at pH 4 − 5 in 0.1 M NaCl and the solubility constant at zero ionic strength is calculated to be $\log_{10} {}^*K^\circ_{s,0} = (9.8 \pm 0.3)$, $\log_{10} K^\circ_{s,0} = -(46.2 \pm 0.3)$. This value is about 0.5 − 1.5 $\log_{10}$-units higher than the values derived from similar solubility studies in earlier papers of this group [1987RYA/RAI], [1991FEL/RAI], [1997RAI/FEL].

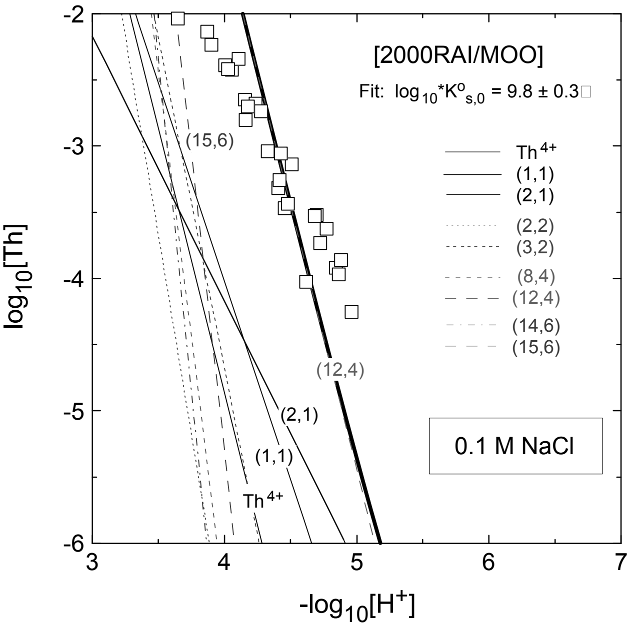
The solubility studies with ThO_2(cr) are performed at low pH where hydrolysis is negligible. As proposed by [2000RAI/MOO] the solubility constant $\log_{10} {}^*K_{s,0}$(0.1 M NaCl, 23°C) ≥ 2.3, derived from data in the pH range 1.3 to 2.0, is considered as a lower limit. Extrapolation to $I = 0$ with the SIT and $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$ kg·mol^{-1} selected by this review gives $\log_{10} {}^*K^\circ_{s,0} \geq 1.0$ ($\log_{10} K^\circ_{s,0} \geq -55.0$) at 23°C.

The solubility constants $\log_{10} {}^*K_{s,0}$ (0.1 M NaCl, 90°C) for ThO_2(cr) and ThO_2(am→cr) are calculated from the experimental values of $\log_{10}[Th^{4+}]$ and pH (activity scale) in the range 1.3 to 2.5 according to:

$$\log_{10} {}^*K_{s,0} = \log_{10}[Th^{4+}] + 4\,(pH + \log_{10} \gamma_{H^+}) \qquad (A.107)$$

with $\log_{10} \gamma_{H^+} = -0.12$ at 90°C. Ionic strength corrections are made with the SIT (*cf.* [1997GRE/PLY2] and [2003GUI/FAN]) using the Debye-Hückel constants *A* and *B* listed in Appendix B of [2003GUI/FAN]. The temperature derivative of the activity of water, $L_1 = -RT^2(\partial \ln a_w / \partial T) = 0.00$ kJ·mol^{-1} for 0.1 M NaCl, and $\varepsilon_L(H^+, Cl^-) = (\partial(\varepsilon(H^+, Cl^-))/\partial T) = -(1.0 \pm 0.1) \cdot 10^{-3}$ kg·mol^{-1}·K^{-1} [1997GRE/PLY2] have no significant effect at $I = 0.1$ M (HCl-NaCl). The unknown value of $\varepsilon_L(Th^{4+}, Cl^-)$ is set equal to zero assuming an uncertainty of $\pm 5 \cdot 10^{-3}$ kg·mol^{-1}·K^{-1}. The following solubility constants, with the uncertainty given as 2σ, are obtained at 90°C: $\log_{10} {}^*K_{s,0}$ (0.1 M NaCl) = (1.3 ± 0.4) and $\log_{10} {}^*K^\circ_{s,0} = -(0.2 \pm 0.4)$ for ThO_2(cr), $\log_{10} {}^*K_{s,0}$ (0.1 M NaCl) = (3.5 ± 0.4) and $\log_{10} {}^*K^\circ_{s,0} = (2.0 \pm 0.4)$ for ThO_2(am→cr).

Figure A-43: Solubility data for ThO_2(am, hyd) at 23°C in 0.1 M NaCl [2000RAI/MOO]: Recalculation of the solubility constant and aqueous speciation using the hydrolysis constants and SIT coefficients selected in the present review.



The solubility constants derived at 23 and 90°C for the different thorium oxides are summarised in Table A-80, together with the values calculated for ThO_2(cr) from thermochemical data and the corresponding solubility constants calculated by Rai *et al.* [2000RAI/MOO]. The solubility constants calculated by this review from the undersaturation solubility experiments with crystalline ThO_2(cr), $\log_{10} K^{\circ}_{s,0} \geq -55.0$ at 23°C and $\log_{10} K^{\circ}_{s,0} = -(49.9 \pm 0.4)$ at 90°C are consistent with the thermochemical values of $\log_{10} K^{\circ}_{s,0} = -(54.2 \pm 1.1)$ at 25°C and $-(51.6 \pm 1.2)$ at 90°C. The solubility constant calculated for the ThO_2(am→cr) phase from solubility data determined at 90°C from oversaturation, after transformation of initially amorphous precipitate into a microcrystalline solid, is 2.2 $\log_{10}$-units higher than the value for crystalline ThO_2(cr) at this temperature. This difference can be attributed to the effect of particle size. The reported X-ray diffraction pattern clearly shows that the crystallite size in the ThO_2(am→cr) phase is much smaller than in the crystalline ThO_2(cr). From the line broadening one can estimate crystallite sizes of $d = (4 \pm 1)$ nm for ThO_2(am→cr) and $d = (17.5 \pm 1.0)$ nm for the crystalline ThO_2(cr) prepared at 750°C. Applying the equation of Schindler (*cf.* Section VII.4.3) to the solubility constant of ThO_2(cr) at 90°C, the variation with particle size d is given by:

$$\log_{10} K^{\circ}_{s,0}\ (\text{ThO}_2, \text{particle size } d) = -(51.6 \pm 1.2) + 21.6 / d(\text{nm}) \qquad (\text{A}.108)$$

Table A-80: Solubility constants $\log_{10} K^{\circ}_{s,0}$ calculated by [2000RAI/MOO] and this review from solubility data for ThO_2(am, hyd), microcrystalline ThO_2(am→cr) and ThO_2(cr) at 23 and 90°C in 0.1 M HCl-NaCl and from thermochemical data for anhydrous ThO_2(cr).

Solid	t (°C)	Method	$\log_{10} K^{\circ}_{s,0}$ [2000RAI/MOO]	$\log_{10} K^{\circ}_{s,0}$ [a] This review (SIT)	$\log_{10} {}^{*}K^{\circ}_{s,0}$ This review (SIT)
ThO_2(am)	23	sol, undersat.	– (44.9 ± 0.5)	– (46.2 ± 0.3)	(9.8 ± 0.3)
ThO_2(cr)	23	sol, undersat.	≥ –56.9	≥ –55.0	≥ 1.0
ThO_2(cr)	90	sol, undersat.	– (51.4 ± 0.2)	– (49.9 ± 0.4)	– (0.2 ± 0.4)
ThO_2(am→cr)	90	sol, oversat.	– (49.2 ± 0.2)	– (47.7 ± 0.4)	(2.0 ± 0.4)
ThO_2(cr)	25	calculated	– 54.2 [c]	– (54.2 ± 1.1)	(1.8 ± 1.1) [b]
	90	calculated	(– 50.8 / – 51.6) [c]	– (51.6 ± 1.2)	– (1.9 ± 1.1) [b]

a: Calculated from $\log_{10} {}^{*}K^{\circ}_{s,0}$ with $\text{p}K^{\circ}_{\text{w}}$ = 14.00 at 25°C and 12.42 at 90°C.

b: Calculated from standard state thermodynamic data for Th(cr), ThO_2(cr) and Th^{4+} selected in the present review. The value at 90°C is calculated according to Eq. (X.19) in [1997ALL/BAN] (Chapter X, p. 434), with a constant value of $\Delta_r C^{\circ}_{p,\text{m}} = -(135 \pm 15)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

c: The thermochemical values calculated by Rai *et al.* [2000RAI/MOO] are based on slightly different thermodynamic data (CODATA, [1976FUG/OET], [1982WAG/EVA]).

Taking into account this dependence on particle size (or better: crystallite size) we calculate a solubility product of $\log_{10} K^{\circ}_{s,0}$ (ThO_2(am→cr), 363 K) = −(46.2 ± 1.9) for the microcrystalline ThO_2(am→cr) phase with d = (4 ± 1) nm and $\log_{10} K^{\circ}_{s,0}$ (ThO_2, cr, 363 K) = −(50.4 ± 1.2) for d = (17.5 ± 1) nm. Both calculated values are, within the uncertainties, consistent with the solubility products derived from the experimental data ($\log_{10} K^{\circ}_{s,0}$ = −(47.7 ± 0.4) and −(49.9 ± 0.4), respectively). However, because of the large uncertainties and because of the fact that the crystallite size estimated above and the particle size in Eq. (A.108) are not identical quantities, these calculations must be considered as semi-quantitative approximations.

[2000THO/DAC]

Normalised leaching rate of thorium phosphate-diphosphate ($Th_4(PO_4)_4P_2O_7$) as a function of temperature, hydrogen ion, and phosphate concentrations are reported. No raw data are available. The leach data are presented in graphical form for the most part as $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and it is reported that $Th_4(PO_4)_4P_2O_7$ is not the equilibrium phase and that the leach rates are governed by thorium phosphate-hydrogen phosphate ($Th_2(PO_4)_2HPO_4\cdot H_2O$). Equilibrium thermodynamic values are not reported, and no experimental data are available to calculate either the solubility products of any of the solids used in the study or the phosphate complexes of thorium.

[2000WAN/GUO]

Using a direct synthesis calorimeter operating at (1473 ± 2) K, these authors determined the enthalpies of formation of $ThAl_2$(cr), $ThSi_2$(cr), $ThGe_2$(cr) and Th_5Sn_3(cr).

The instrument used was a single-unit differential microcalorimeter described in detail in an earlier publication [1989KLE/TOP]. The calibration of the calorimeter was achieved by dropping high purity copper wires from room temperature (298.15 K) into the calorimeter at its working temperature and using literature value for the enthalpy of copper [1973HUL/DES]. Results were reproducible within 1%. All experiments were conducted in an atmosphere of argon from which traces of oxygen and nitrogen had been eliminated by passing it over a titanium sponge at 1173 K. The actual calorimetric syntheses were carried out in boron nitride crucibles. 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.

Samples for calorimetry were prepared by mixing the two component powders, accurately weighed according to the appropriate stoichiometry, and pressing the mixture into 4 mm diameter pellets. The purity of the commercial materials used was given as 99.5% for Si and Al, 99.8% for Th, 99.995 for Ge and 99.999% for Sn, without further details. The authors mention precautions in handling the easily oxidised thorium metal powder. X-ray diffraction measurement suggested that the thorium samples might contain up to 3.5% ThO_2. However, this value could be considered as an upper limit representing the outer layers of the thorium powder (100 mesh size), given the low penetration of the X-rays into the thorium metal. X-ray examination of the samples after calorimetric reaction showed, for all compounds for which an enthalpy of formation was reported, the absence of unreacted materials. About 5% of ThO_2 were detected in all compounds. In the case of $ThAl_2$, minor amounts of $ThAl_3$ were detected. For $ThSi_2$, three weak unknown peaks were detected. For Th_5Sn_3, minor quantities of Th_5Sn_4 were identified. In the absence of standard X-ray diffraction patterns for the Th-Sn alloys in the ASTM powder diffraction file, the authors resorted to a commercial software program to obtain ideal diffraction patterns for the various compounds in the Th-Sn system. In the case of $ThGe_2$, no extraneous lines could be identified, although the authors report that their compound did not match the standard X-ray diffraction pattern for this compound, or for any other Th-Ge compound.

The calorimetric results are the average of four to six individual measurements and the overall uncertainties on the results are reported as the combined standard deviation taking in account the uncertainties of the calibration runs and are given as:

$$\Delta_f H_m^o (\text{ThAl}_2, \text{cr}, 298.15\ \text{K}) = -(140.4 \pm 6.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^o (\text{ThSi}_2, \text{cr}, 298.15\ \text{K}) = -(166.8 \pm 6.0)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^o (\text{ThGe}_2, \text{cr}, 298.15\ \text{K}) = -(216.6 \pm 4.2)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^o(\mathrm{Th_5Sn_3, cr, 298.15\ K}) = -(510.4 \pm 16.0)\ \mathrm{kJ \cdot mol^{-1}}.$$

The authors discuss their results in the light of values predicted by semi-empirical models for intermetallic compounds and with earlier experimental literature results for the enthalpy of formation of these and related compounds.

[2001ALI/MIS]

The authors measured the pressure of Sr(g) obtained by heating $SrThO_3$(cr) in a tungsten cell from 1677 to 2419 K by mass loss Knudsen effusion. X-ray examination of the residue after partial decomposition showed that the condensed phases were different in different temperature ranges. As well as $SrThO_3$(cr), W(cr) and ThO_2(cr), Sr_2WO_5(cr) was present from 1677 to 2047 K, but $SrWO_4$(cr) was found in experiments from 2138 to 2419 K. Since $SrWO_4$ would be molten at these higher temperatures, Energy Dispersive X-ray analysis was carried out to determine whether there was any solubility of thorium species in this melt. Less than 10% ThO_2 was detected, but the authors were not clear whether this was due to dissolution of *e.g.* $SrThO_3$ or from interference from neighbouring ThO_2 particles. Thus $SrWO_4$(l) was treated as a pure phase in the subsequent analysis, as was ThO_2(cr), although the solubility of SrO in ThO_2 (cr) at 2273 K is reported to be as high as 13 mol%. The uncertainty resulting from these assumptions was estimated by the authors to be 2.6 kJ·mol^{-1}. The authors discuss and dismiss the possible loss of oxygen to form phases containing lower-valent tungsten, such as $SrWO_3$(cr).

The relevant reactions were thus assumed to be:

$$5\mathrm{SrThO_3(cr)} + \mathrm{W(cr)} \rightleftharpoons \mathrm{Sr_2WO_5(cr)} + 5\mathrm{ThO_2(cr)} + 3\mathrm{Sr(g)} \quad 1677\ \text{to}\ 2047\ \mathrm{K} \quad (A.109)$$

and

$$4\mathrm{SrThO_3(cr)} + \mathrm{W(cr)} \rightleftharpoons \mathrm{SrWO_4(l)} + 4\mathrm{ThO_2(cr)} + 3\mathrm{Sr(g)} \quad 2138\ \text{to}\ 2419\ \mathrm{K} \quad (A.110)$$

Measurements were also made below 1670 K, but the establishment of the equilibrium (probably with Sr_3WO_6(cr)) was too slow for the results to be reliable. The $SrThO_3$ solid was prepared by "sol-gel combustion" as described by [2000PUR/TYA]. This involves heating the nitrates of strontium and thorium with citric acid, which acts as an ignition agent. X-ray diffraction showed the presence of a monoclinic cell with parameters in good accord with other determinations [2000PUR/TYA], [1947NAR]. The calculated decomposition pressures for Reactions (A.109) and (A.110) are well represented by the equations $\log_{10} p_{\mathrm{Sr}}/\mathrm{bar} = -19291/T + 5.280$ and $\log_{10} p_{\mathrm{Sr}}/\mathrm{bar} = -21719/T + 6.166$. The Gibbs energy of the above reactions are thus

$$\Delta_r G_m((A.109), T) = 1107989 - 303.240\,T \quad (\mathrm{J \cdot mol^{-1}})$$

and $$\Delta_r G_m((A.110), T) = 1247401 - 354.041\,T \quad (\mathrm{J \cdot mol^{-1}}).$$

The Gibbs energy of the reaction $\mathrm{Sr(g)} + 0.5\mathrm{O_2(g)} \rightleftharpoons \mathrm{SrO(cr)}$ over the experimental temperature range is given by $-726189 + 185.253\,T$ (J·mol^{-1}), where the data are taken from the recent assessment by [1994GUR/VEY], adjusted slightly to accord with Table IV-1. The only experimental data for the Gibbs energies of formation of $SrWO_4(cr)$ and $Sr_2WO_5(cr)$ are those for the reactions:

$$SrO(cr) + W(cr) + 1.5O_2(g) \rightleftharpoons SrWO_4(cr), \quad \Delta_r G_m = -1031495 + 234.443\,T\ (J\cdot mol^{-1})$$

and

$$2SrO(cr) + W(cr) + 1.5\,O_2(g) \rightleftharpoons Sr_2WO_5(cr), \quad \Delta_r G_m = -1090350 + 246.019\,T\ (J\cdot mol^{-1})$$

given by Levitskii and Skolis [1974LEV/SKO] for temperatures from 1100 to 1500 K, based on emf measurements. These have been assumed to apply at the appreciably higher temperatures of the current experiments. For Reaction (A.110), we also require the Gibbs energy of fusion of $SrWO_4$, which is not known. The authors used an estimated enthalpy of fusion of 30 $kJ\cdot mol^{-1}$, which we have accepted together with the melting point of 1808 K, giving $\Delta_{fus}G_m$ $(SrWO_4) = 30000 - 16.593\,T\ (J\cdot mol^{-1})$. Manipulation of the appropriate equations gives for the Gibbs energy of the formation reaction of $SrThO_3(cr)$ from the component oxides:

$$SrO(cr) + ThO_2(cr) \rightarrow SrThO_3(cr) \qquad (A.111)$$

$[\Delta_r G_m]_{1670K}^{2040K}$ ((A.111), T) $= -3955 - 1.300\,T\ (J\cdot mol^{-1})$ from Reaction (A.109), and

$[\Delta_r G_m]_{2135K}^{2420K}$ ((A.111), T) $= -17583 + 4.033\,T\ (J\cdot mol^{-1})$ from Reaction (A.110)

Considering the extrapolations involved, and the uncertain activities for Reaction (A.110), it is not surprising the enthalpy and entropy values differ, but in fact the Gibbs energy of the formation reaction from the oxides at the intermediate temperature 2100 K, $-(6.7 \pm 4.0)$ and $-(9.1 \pm 10.0)$ $kJ\cdot mol^{-1}$ agree remarkably well. The uncertainties are those estimated by the authors.

This is a lower stability than $BaThO_3(cr)$ but is appreciably more negative than the trends in the actinide(IV) mixed oxides would suggest. Indeed [1993FUG/HAI], estimated $\Delta_r H_m^\circ$ ((A.111), 298.15 K) to be $+(20.0 \pm 8.5)$ $kJ\cdot mol^{-1}$, and Smith and Welch [1960SMI/WEL] were unable to prepare $SrThO_3$ by heating a mixture of $ThO_2(cr)$ and $SrCO_3(cr)$ in air at 1273 to 1923 K and suggested that the XRD pattern attributed to $SrThO_3(cr)$ by [1947NAR] fitted better to the two components $SrO(cr)$ and $ThO_2(cr)$. Similarly, Smith and Welch indicated that the diffraction pattern given by [1947NAR] for his reported $CaThO_3(cr)$ agrees well with that for a mixture of ThO_2 and hydrated lime. Keller [1976KEL] has also thrown doubt on some of the results of [1947NAR].

Although the sol-gel technique provides intermediate products of much smaller particle size, and thus more readily reactive, we also note that no detailed analyses to confirm the positive identification of the final product as $SrThO_3(cr)$ were made by either [2000PUR/TYA] or [2001ALI/MIS]. We also note the equation given by the authors for $\Delta_r G_m$ (A.111) from Reaction (A.109), based on different auxiliary data, $\Delta_r G_m$ ((A.111), T) $= -4900 + 3.0\,T\ (J\cdot mol^{-1})$ would actually make $SrThO_3(cr)$, metastable with respect to the component oxides in the temperature range of their experiments.

The data from Reaction (A.109) are the less uncertain; these correspond to the Gibbs energy of formation from the elements: $[\Delta_f G_m]_{1670\text{K}}^{2040\text{K}}$ ($SrThO_3$, cr, T) = − 194680 + 36.23 T, where the standard state for strontium in this temperature range is Sr(g). However, owing to the uncertainties in the assessment noted above and in the identification of $SrThO_3$(cr), these data are given for information only.

[2001BEE/DYK]

Ultraviolet photoelectron spectra of UBr_4 and $ThBr_4$ were recorded in the gas phase and interpreted using relativistic density functional calculations. Supporting matrix isolation infrared experiments were also carried out under very similar vaporisation conditions to those used in the photoelectron spectroscopy experiments to check the composition of the vapour beams used. In these experiments, the T_2 stretching modes of $ThBr_4$ and UBr_4 have been measured to be (230 ± 2) and (239 ± 2) cm^{-1}, respectively. Both the photoelectron and infrared matrix isolation spectra are consistent with an effective tetrahedral geometry for UBr_4(g) and $ThBr_4$(g).

[2001BRA/DAC]

This review paper deals with the syntheses of uranium and thorium phosphates and discusses at length the syntheses of $Th_4(PO_4)_4P_2O_7$ for storing radioactive wastes. No thermodynamic data are reported.

[2001BRA/DAC2]

The authors report the syntheses of $Th_2(PO_4)_2HPO_4\cdot H_2O$ and $Th(OH)PO_4$ from aqueous solutions under hydrothermal conditions at temperatures around 150°C. A combination of techniques (SEM, XRD, IR, electron probe microanalyses, DTA and TGA) are used. It is indicated that the dissolution reactions of $Th_4(PO_4)_4P_2O_7$ in water results in the formation of $Th_2(PO_4)_2HPO_4\cdot H_2O$. No original thermodynamic data were obtained in this study.

[2001HUB/BAR]

Hubert *et al.* [2001HUB/BAR] performed leaching experiments with crystalline ThO_2(cr) in 0.1 M $HClO_4$-$NaClO_4$ at room temperature (assumed to be 20−25°C). Aqueous thorium concentrations were determined by ICP-MS after phase separation by ultracentrifugation The solids used were prepared from different precursors (hydroxide, nitrate and oxalate) and calcined at different temperatures (600, 900, 1300 and 1600°C). This resulted in different properties (specific surface area, surface state, size of aggregates) that govern the dissolution kinetics. As previously reported by Greiling and Lieser [1984GRE/LIE], who studied the dissolution kinetics of ThO_2(cr) in 7.5 M HNO_3, using solids prepared by calcination of hydroxide and oxalate precipitates at 450 to 1400°C, increasing calcination temperature and the use of thorium oxalate as a precursor leads to lower specific surface area and lower dissolution rates in acidic solution. For the solids studied by [2001HUB/BAR] at pH 1 to 3, equilibrium was not reached after 123 days.

Contrary to the data at low pH, the Th concentrations measured at pH 5.3 − 7.2 after only 10 days are already orders of magnitude higher than $\log_{10}[\mathrm{Th}] = \log_{10} K^{\circ}_{s,4}$ (ThO_2, cr) = −(15.6 ± 1.3) as calculated for the reaction:

$$ThO_2(cr) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq)$$

using $\Delta_f G^{\circ}_m$ (ThO_2, cr, 298.15 K) = −(1169.0 ± 3.5) kJ·mol^{-1} ($\log_{10} {}^*K^{\circ}_{s,0}$ (ThO_2, cr, 298.15 K) = (1.77 ± 1.11)) and $\log_{10} {}^*\beta^{\circ}_{4,1}$ = −(17.4 ± 0.7) selected by this review. The mean values of $\log_{10}[\mathrm{Th}]$ extracted from Figure 4 of [2001HUB/BAR] for ThO_2(cr) prepared from hydroxide (−(10.3 ± 0.2)), nitrate (−(9.6 ± 0.4)) and oxalate (− (10.6 ± 0.6)) at 900 and 1600°C are close to experimental $\log_{10} K_{s,4}$ values for amorphous hydroxides or hydrous oxides ThO_2(am, hyd).

[2001MOU/AME]

This is an interesting article describing the use of electrospray-ionisation mass spectrometry for the identification of hydroxide complexes of Th(IV). The method involves injection of 1 mM Th(IV) solutions in 1, 0.1, 0.01 and 0.001 M $HClO_4$ through an electro-spray nozzle into the high-vacuum system of a mass spectrometer where a rapid evaporation takes place and the ions formed are analysed in a quadrupole mass spectrometer. The authors briefly describe the methodology and discuss various factors that might affect the interpretation of the resulting mass spectra. The ions formed have a charge of + 1 and their stoichiometry can be identified by their mass and their relative amounts by the intensity of the peaks in the mass spectra. The authors demonstrate that the mass distribution varies with the speciation in the injected solution, indicating that the method might be useful as a speciation probe and even to obtain equilibrium information. From the mass spectra they find that the following stoichiometry for the major peaks:

- At pH = 0: $Th(ClO_4)_3(H_2O)_3^+$, indicating a coordination number of 9 for Th^{4+}, assuming bidentate coordination of perchlorate.
- At pH = 2: $Th(ClO_4)_3(H_2O)_3^+$; $Th(OH)(ClO_4)_2(H_2O)_2^+$ and $Th(OH)(ClO_4)_2(H_2O)_3^+$; the latter indicating coordination numbers of seven and eight.
- At pH = 3: $Th(OH)_2(ClO_4)(H_2O)^+$; $Th(OH)_2(ClO_4)(H_2O)_2^+$, with coordination numbers of five and six.

It is interesting to note that the species at pH = 0 and 2 seem to have coordination numbers that are consistent with those found in solution and the solid state. There is also a quantitative estimate of the relative amounts of different species that was used to estimate equilibrium constants for the formation of $\mathrm{Th(OH)^{3+}}$, $\mathrm{Th(OH)_2^{2+}}$ and $\mathrm{Th(OH)_3^{+}}$. These values are $\log_{10} {}^*\beta^{\circ}_{n,1}(\mathrm{Th(OH)}_n^{4-n}) = -(2.0 \pm 0.2)$, $-(4.5 \pm 0.5)$ and $-(7.5 \pm 1.0)$ for $n = 1$, 2 and 3, respectively. These values, in particular $\log_{10} {}^*\beta^{\circ}_{2,1}$ and $\log_{10} {}^*\beta^{\circ}_{3,1}$, differ appreciably from those determined by other methods, which is not surprising. At the present stage this method does not seem to provide quantitative equilibrium information, but it seems to have the potential for identification of possible hydrolytic species.

[2001NEC/KIM]

The authors review the solubility and hydrolysis of tetravalent actinides using experimental data and semi-empirical estimates among the series of tetravalent actinides Th(IV), U(IV), Np(IV) and Pu(IV). They present a set of selected equilibrium constants that are based preferentially on experimental data using trace concentration of the actinides. The rationale for this is based on experience of studies of colloid formation using laser-induced breakdown detection [1999KNO/NEC], [2000BUN/KNO], [2001NEC/KIM2], [2002NEC/MUL].

The authors also use semi-empirical methods to estimate the equilibrium constants for mononuclear An(IV) hydroxide complexes. Two methods are suggested: Model A assumes a linear correlation between the formation constants $\log_{10} \beta^{\circ}_{n,1}(\mathrm{ML}_n)$ and the ion potential $Z/d_{\mathrm{An-OH}}$, while Model B is based on an electrostatic approach described in detail in [2000NEC/KIM]. The model assumes a relationship between the consecutive equilibrium constants of the form:

$$\log_{10} \beta^{\circ}_{n,1} = n \log_{10} \beta^{\circ}_{1,1} - {}^{\mathrm{rep}}E_{\mathrm{L}}/\mathrm{R}T\ln 10$$

where

$${}^{rep}E_L = N_A\, e^2 \left(1/2\right) \sum_L \frac{z_L z_{L'}}{d_{L-L'}\,\varepsilon_{L-L'}}$$

N_A is Avogadro's number, e the electron charge, Z_L and $Z_{L'}$ the charges of ligands L and L', $d_{L-L'}$ the distance between the centres of the two ligands calculated from the distance between M and L and the geometry of the complex (octahedral, tetrahedral *etc.*), $\varepsilon_{L-L'}$ is a factor describing the electrostatic shielding between the ligands L and L' that is determined by fitting a "virial" equation. The present review does not select equilibrium constants based on correlations of this type, but [2001NEC/KIM] provides an important discussion of the chemistry of tetravalent actinides (*cf.* [2003GUI/FAN]).

The authors note that potentiometric studies performed with Th(IV) by different authors are interpreted by different sets of species and ascribe this to colloid formation. The present review does not share this opinion, precise potentiometric data, $\bar{n}_{\mathrm{OH}}$ ($\log_{10}[\mathrm{H^+}]$), agree very well with each other if obtained by specialists, provided the same ionic medium is used, *cf.* [1964HIE/SIL] and [1965BAE/MEY]. Neck and Kim [2001NEC/KIM] select hydrolysis constants and ion interaction (SIT) coefficients for the Th(IV) hydroxide complexes $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_4(OH)_8^{8+}}$, $\mathrm{Th_4(OH)_{12}^{4+}}$, and $\mathrm{Th_6(OH)_{15}^{9+}}$ from the potentiometric titration studies of Baes *et al.* [1965BAE/MEY], [1976BAE/MES], Brown *et al.* [1983BRO/ELL], Grenthe and Lagerman [1991GRE/LAG2], and Ekberg *et al.* [2000EKB/ALB]. The equilibrium constants for the mononuclear species $\mathrm{Th(OH)_3^+}$, $\mathrm{Th(OH)_2^{2+}}$ and $\mathrm{Th(OH)^{3+}}$ are taken from the potentiometric and solvent extraction studies of [1983BRO/ELL], [1984NAK/ZIM], [2000EKB/ALB] and the semi-empirical estimates discussed above. The SIT coefficients for the mononuclear species were estimated according to charge type analogies and systematics in the actinide series. The equilibrium constant for $\mathrm{Th(OH)_4(aq)}$ is derived from the pH-independent solubility of Th(IV) hydrous oxide at pH to 14 [1987RYA/RAI], [1989MOO], [1991FEL/RAI]: $\log_{10} K^{\circ}_{s,4} = -(8.5 \pm 0.6)$.

Using these hydrolysis constants and ion interaction coefficients listed in Table A-81, Neck and Kim re-evaluated the solubility data reported by [1964NAB/KUD], [1987RYA/RAI], [1989MOO], [1991FEL/RAI] at 17 to 25°C and calculated a mean value of $\log_{10} K^{\circ}_{s,0}$ ($\mathrm{Th(OH)_4}$, am) = $-(47.0 \pm 0.8)$ ($\log_{10} {}^{*}K^{\circ}_{s,0}$ ($\mathrm{Th(OH)_4}$, am) = (9.0 ± 0.8)). The solubility constant for $\mathrm{ThO_2(cr)}$, $\log_{10} K^{\circ}_{s,0}$ ($\mathrm{ThO_2}$, cr, 298.15 K) = $-(54.2 \pm 1.3)$ is adopted from Rai *et al.* [1987RAI/SWA] and based on thermochemical data which are only slightly different from those selected in the present review.

An important observation discussed in [2001NEC/KIM] is that experimental solubility data in neutral and alkaline solutions are approximately the same for amorphous hydroxides $\mathrm{An(OH)_4}$(am, hyd) or hydrous oxides $\mathrm{AnO_2}$(am, hyd) and crystalline oxides $\mathrm{AnO_2(cr)}$, although their solubility constants differ by 6−7 orders of magnitude. Solubility data determined with $\mathrm{AnO_2(cr)}$ at pH > 5 do not reflect an equilibrium with the bulk solid but with amorphous fractions or an amorphous surface layer.

Table A-81: Hydrolysis constants $\log_{10} {}^{*}\beta^{\circ}_{n,m}$ at zero ionic strength and ion interaction (SIT) coefficients ε_{ij} ($\mathrm{kg \cdot mol^{-1}}$) selected in [2001NEC/KIM]. (In this paper the equilibrium constants $\log_{10} \beta^{\circ}_{n,m}$ have been reported for the reactions $m\mathrm{Th^{4+}} + n\mathrm{OH^-} \rightleftharpoons \mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}$).

$\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}$	$\log_{10} {}^{*}\beta^{\circ}_{n,m}$	$\varepsilon(\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}, \mathrm{ClO_4^-})$	$\varepsilon(\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}, \mathrm{Cl^-})$
$\mathrm{Th^{4+}}$	–	0.67 ± 0.1	0.25 ± 0.03 [b]
$\mathrm{Th(OH)^{3+}}$	-2.2 ± 0.2	0.45 ± 0.1	0.2 ± 0.1 [c]
$\mathrm{Th(OH)_2^{2+}}$	-6.0 ± 0.6	0.3 ± 0.1	0.1 ± 0.1 [c]
$\mathrm{Th(OH)_3^{+}}$	-11.0 ± 1	0.15 ± 0.1	0.05 ± 0.1 [c]
$\mathrm{Th(OH)_4(aq)}$	-17.5 ± 1	0	0
$\mathrm{Th_2(OH)_2^{6+}}$	-5.7	1.3	
$\mathrm{Th_4(OH)_8^{8+}}$	-20.4	1.7	
$\mathrm{Th_4(OH)_{12}^{4+}}$	-26.7	0.4	
$\mathrm{Th_6(OH)_{15}^{9+}}$	-34.0	5.6 ± 1.9	

[2001THO/DAC]

The authors have studied the rate of dissolution of solid solutions of U(IV) and Th(IV) phosphate phases. The paper contains information on the proposed dissolution mechanism and also extensive information on phase characterisation. Of particular interest is the solid $Th_2(PO_4)_2(HPO_4)\cdot H_2O$; this pure phase and the solid solutions were characterised using XRD, IR, UV-visible spectrophotometry, electron probe microanalysis, SEM and TEM. There is no thermodynamic information on the pure $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ phase except for a value of its solubility product at zero ionic strength, $\log_{10} K^{\circ}_{s,0} = -(66.6 \pm 1.2)$ for which a reference is given to a forthcoming publication; as this is not available to the present review this solubility product is not accepted.

[2001VEN/NAG]

The authors measured the heat capacity of $BaThO_3$(cr) from *ca.* 320 to 820 K by DSC. The $BaThO_3$ solid was prepared by combustion synthesis from the nitrates of barium and thorium using citric acid as an ignition agent, initially by heating to 573 K, then to 1173 K to remove residual carbon and hydrogen, with final homogenisation at 1673 K for 60 hours. The product was described as single-phase $BaThO_3$(cr), as characterised by X-ray diffraction. Absolute values of the heat capacity were obtained by using sapphire as a standard. The heat capacity of ThO_2(cr) was also measured as a check; the values obtained were in good agreement with the assessment by [1997BAK/COR], and thus with the selected values. The results of 26 measurements were fitted to the expression:

$$[C_{p,\mathrm{m}}]_{320\mathrm{K}}^{820\mathrm{K}}(\mathrm{BaThO_3, cr}, T) = 137.9046 + 5.272\times10^{-2}\,T - 2.432487\times10^{6}\,T^{-2}\quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

However, this corresponds to a large $\Delta_f C_{p,\mathrm{m}}$ of the formation reaction from the solid oxides in the range of temperature measurement; the calculated values for this $\Delta_f C_{p,\mathrm{m}}$ are 20.0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 320 K and 50.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 820 K; even larger values would be obtained by extrapolation of the equation to higher temperatures. These large values must throw doubt on the validity of the results and these data are mentioned for information only.

[2001YAN/TSU]

This paper of Yang *et al.* is discussed together with [2002YAN/TSU].

Both these papers describe the use of quantum chemical and molecular dynamics simulations to study the structure of the first and second coordination spheres of Th(IV) and to determine the residence time of water in the second coordination sphere. In the second paper the authors discuss the entry of chloride into the second coordination sphere at different concentrations of chloride. The starting point in these studies is the determination of the geometry and relative energy of different hydration isomers of Th(IV) using *ab initio* quantum mechanics. When the ratio $(H_2O)/(Th^{4+})$ is nine, the most stable structure, $[\mathrm{Th(H_2O)_9^{4+}}]$ has a C_{4v} geometry (a capped square antiprism), followed by $[\mathrm{Th(H_2O)_9^{4+}}]$ with a D_{2d} geometry (a bicapped trigonal prism) 17 kJ·mol^{-1} higher in energy. The least stable isomer $[\mathrm{Th(H_2O)_8^{4+}}]$,$(\mathrm{H_2O})$ has a C_{2v} geometry and an energy that is 52 kJ·mol^{-1} above the C_{4v} isomer; this isomer is eight-coordinated with one water in the second coordination sphere. The most stable structure when the ratio $(\mathrm{H_2O})/(\mathrm{Th^{4+}})$ is ten, is $[\mathrm{Th(H_2O)_9^{4+}}]$,$(\mathrm{H_2O})$ with C_{4v} geometry (a capped square antiprism), followed by $[\mathrm{Th(H_2O)_{10}^{4+}}]$ only 3 kJ·mol^{-1} higher in energy; the latter has D_{4d} geometry. The other isomers are significantly higher in energy. The structure and dynamics of the second (and third) coordination spheres are studied using molecular dynamics (the AMBER code) with the hydrated ion concept, assuming the $[\mathrm{Th(H_2O)_9^{4+}}]$ geometry and describing the interaction potential between this unit and surrounding solvent molecules using empirical potentials (one Coulomb and one Lennard-Jones part). The calculated $\mathrm{Th^{4+}}$–$\mathrm{OH_2}$ distance is in good agreement with experimental data [1991JOH/MAG], [1999MOL/DEN] where the concentration used in [1991JOH/MAG] is closer to the conditions used in the simulations. The second coordination sphere contains 18.9 water molecules with a residence time of 423 picoseconds; the number of second sphere water molecules is in good agreement with that in [1991JOH/MAG]. By increasing the number of chloride ions in the simulations the authors investigated the conditions under which water in the second coordination sphere can be replaced by chloride. At room temperature chloride enters the second coordination sphere only when the chloride concentration is around 2.6 m. In this simulation it was assumed that chloride did not enter the first coordination sphere, an assumption supported by the experimental results of Johansson *et al.* [1991JOH/MAG], who found that chloride entered the first coordination sphere only at very high concentrations, 7.4 M. Entry of chloride in the second coordination sphere also resulted in a shortening of the residence time of water. The most important conclusion of these two studies is that they establish the coordination number and coordination geometry of the Th(IV) aquo ion to be $[\mathrm{Th(H_2O)_9^{4+}}]$ or $[\mathrm{Th(H_2O)_{10}^{4+}}]$ with a coordination geometry based on a capped square antiprism. It is also of interest to note that if the coordination geometry is $[\mathrm{Th(H_2O)_9^{4+}}]$ the exchange of water between the first and second coordination sphere is most likely associative; the energy difference between the ground state and the associative intermediate is 3 kJ·mol^{-1} and that between the ground state and the dissociative intermediate 52 kJ·mol^{-1}. If the coordination in the ground state is $[\mathrm{Th(H_2O)_{10}^{4+}}]$, the water exchange is dissociative as suggested by Farkas *et al.* [2000FAR/GRE].

The second sphere residence times in $(\mathrm{Th(H_2O)_9^{4+}})$ and $(\mathrm{Th(H_2O)_{10}^{4+}})$ are very different, 398 ps *vs.* 1500 ps; if the residence time could be determined experimentally this would offer a possibility to determine the coordination number. On the other hand equilibrium between isomers with two different coordination numbers is also possible.

[2002ABD]

The study describes the solubility of monazite in aqueous solutions of ammonium carbonate/bicarbonate at different pressure and temperature. The recovery of Th(IV) in the leach process is surprisingly high, ranging from 18.7% at 70°C to 99.8% at 150 to 175°C. These observations confirm the formation of strong carbonate complexes. However, there are no quantitative thermodynamic data in this communication.

[2002BRA/DAC]

The authors report the syntheses of several different thorium phosphate solids ($ThFPO_4 \cdot H_2O$, $Th_2(PO_4)_2SO_4 \cdot 2H_2O$, $Th_4(PO_4)_4SiO_4$, $CsTh_2(PO_4)_3$, $BaTh(PO_4)_2$) from aqueous solutions under hydrothermal conditions. The chemical composition of the solids was established by electron probe microanalysis and/or particle induced X-ray emission. The X-ray diffraction patterns and/or infrared spectra were given. No thermodynamic data are reported.

[2002DAC/CHA]

This work is part of a broad effort to evaluate the potential of phosphate matrices for radioactive waste storage. It concerns the synthetic methods for preparing $Th_4(PO_4)_4P_2O_7$, thorium phosphate diphosphate (TPD) and the study of its physical, thermal, and thermomechanical properties and chemical durability during leaching tests. Only the determination of the specific heat of the compound between room temperature and 1073 K is of relevance to this review. These measurements were made in an argon atmosphere on powdered samples in an alumina holder using a Setaram Differential Scanning Calorimeter (model 111), with calibration against sapphire provided by NIST as a reference material. Data were taken between 293 and 1073 K, with steps of 20 K and an acquisition time of 600 s. The heating rate between two steps was 5 $K \cdot min^{-1}$. Individual experimental values were given only on a C_p *vs.* T graph. The equation for the fit to the specific heat in the text seems to be in error, and we have refitted the original values of the specific heat, kindly provided by the authors,

$$C_p = 0.46262 + 6.94205 \times 10^{-5}\,T - 1.2367 \times 10^{-10}\,T^2 - 9402.0\,T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$$

which for a molecular weight of 1505.981 corresponds to the molar heat capacity equation:

$$[C_{p,\text{m}}]_{298.15\text{K}}^{1073\text{K}} = 696.70 + 0.10455\,T - 1.8625 \times 10^{-7}\,T^2 - 1.4159 \times 10^{7}\,T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

[2002FAN/NEC]

The authors discuss systematic trends and specific phenomena on the solubility of hydroxides and oxides of tri-, tetra-, penta- and hexavalent actinides. The reported solubility constants of amorphous ThO_2(am, hyd), microcrystalline and crystalline ThO_2(cr), the conclusions on the solubility controlling solid phase and the solubility increasing effect of eigencolloids are taken from [2001NEC/KIM], [2002NEC/MUL], [2003NEC/ALT]. Experimental solubility constants of Th(IV) oxides/hydroxides of different crystallinity are illustrated as a function of particle size in comparison with calculations based on Schindler's equation [1967SCH].

Experimental data are discussed in the Appendix A reviews of [2001NEC/KIM], [2002NEC/MUL], [2003NEC/ALT].

[2002JER/VUO]

In this report the solubility of thorium was investigated in 0.1 M NaCl solution and in saline and fresh anoxic synthetic reference groundwater (I = 0.5 and 0.002 M, respectively, major electrolyte: NaCl) containing 10^{-6} to 10^{-5} M total carbonate. Different sets of solubility experiments in the pH range of 6 to 13 were performed at 20.5 − 23°C from oversaturation and, with $ThO_2{\cdot}xH_2O(s)$ prepared and dried as described by Östhols *et al.* [1994OST/BRU], from undersaturation. The solid phases were studied by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD patterns showed slight indications of microcrystalline fractions. The low carbonate concentrations of $10^{-5} - 10^{-6}$ M have no effect on the solubility and aqueous thorium speciation, but IR spectrometry gave an indication that carbonate might be sorbed onto the solid phase.

The samples were kept in an inert gas glove box and equilibrated for 10 to 200 days. The thorium concentration was determined by ICP-MS after phase separation by centrifugation or 450 nm pre-filtration and subsequent 50000 MWCO (Molecular Weight Cut-Off) ultrafiltration and pH was measured with a combination electrode calibrated against commercial pH buffers. Nearly all the 42 solubility data in the different solutions and at different pH values were in the range $10^{-10} - 10^{-8}$ M. There is no significant effect of pH and equilibration time.

If the mean value of the measurements in [2002JER/VUO], $\log_{10}[\text{Th}] = -(9.5 \pm 1.2)$ (2σ), is ascribed to the reaction $ThO_2(\text{am, hyd}) + 2H_2O \rightleftharpoons Th(OH)_4(aq)$ and combined with the solubility constant of a ThO_2(am, hyd) solid prepared and pretreated the same way ($\log_{10} {}^{*}K^{\circ}_{s,0} = (8.2 \pm 0.6)$, calculated by this review from the solubility data of [1994OST/BRU] and [2002NEC/MUL] at pH 3.2−4.5), we obtain the hydrolysis constant of $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ ($Th(OH)_4$, aq) = −(17.7 ± 1.3). This value agrees with the $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ values calculated by this review from solubility studies of other authors (− (17.6 ± 0.6) [1987RYA/RAI], −(17.6 ± 0.4) [1989MOO], −(17.2 ± 1.2) [1991FEL/RAI], − (16.9 ± 1.0) [2002NEC/MUL], [2004ALT/NEC]).

[2002JOS/SIV]

Partial pressures of different species present in the vapour phase over ThO_2, UO_2, UC, were studied at very high temperature (>3000 K), by transient heating of the sample with a 532 nm laser pulse of *ca.* 8 ns duration with time-resolved mass-spectrometric detection. The surface temperature was varied by changing the laser incident power on the sample. For ThO_2, the authors give partial pressures of Th(g), ThO(g), ThO_2(g) and O(g) at 5146 and 6253 K. Since in this type of experiment, it is difficult to establish reliably the relevant temperatures, these data have not been used in the analysis. Nevertheless, the extrapolation of these data down to the melting point of ThO_2 (3650 K), gives a value in good agreement with the selected data, extrapolated upwards.

This study gives the first information on the vaporisation of thoria at very high temperatures.

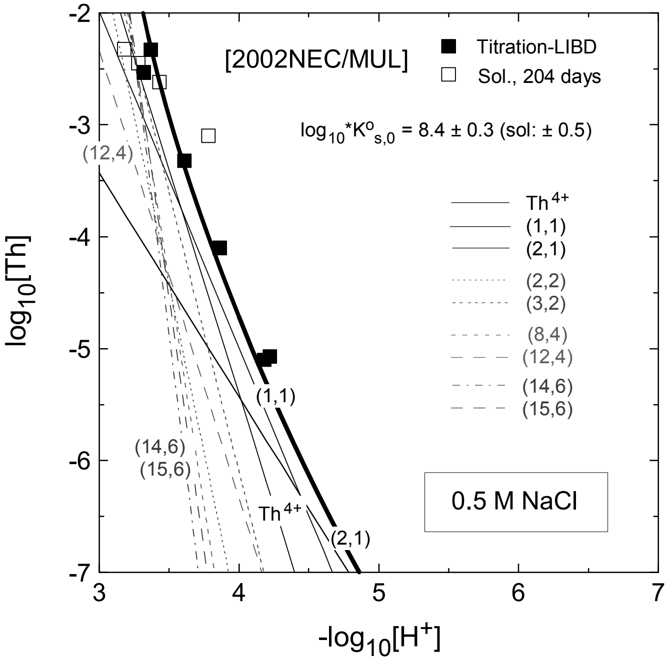
[2002NEC/MUL]

Neck *et al.* [2002NEC/MUL] studied the solubility of amorphous Th(IV) hydrous oxide at pH 3.0 − 13.5 in 0.5 M NaCl and 25°C. The authors performed solubility measurements with $ThO_2{\cdot}xH_2O(am)$ from undersaturation (equilibration times: 5 − 211 days) and used laser-induced breakdown detection (LIBD) to detect the initial formation of thorium hydroxide colloids during the coulometric titration of $10^{-2} - 10^{-5}$ M thorium solutions in the $-\log_{10}[H^+]$ range 2.7 − 4.5. The temperature and ionic medium were the same as in [2000BUN/KNO]. The experimental solubility product given by the authors, $\log_{10} K_{s,0} = -(44.48 \pm 0.24)$ and $\log_{10} K^{\circ}_{s,0} = -(47.8 \pm 0.3)$, is much larger than that obtained for ThO_2 colloids in acid solution ($-(52.8 \pm 0.3)$) [2000BUN/KNO], and corresponds to the solubility products obtained for amorphous thorium hydroxide phases. There are other important observations in this study: colloids that were formed in the coulometric experiment as a result of local excess of hydroxide redissolved if outside the stability region for colloid formation; similar observations have been made in previous potentiometric titrations.

When evaluating the solubility product in the investigated $-\log_{10}[H^+]$ region it is necessary to take the formation of hydroxide complexes into account. The authors have used the hydrolysis constants and SIT coefficients selected in the literature review of [2001NEC/KIM] (*cf.* Table A-81). As seen in Figure 4 of [2002NEC/MUL], the complex $Th(OH)^{3+}$ is predominant in the test solutions and the selected hydrolysis constants, in particular the value of $\log_{10} {}^*\beta^{\circ}_{1,1} = -2.2$ (which is higher than $\log_{10} {}^*\beta^{\circ}_{1,1} = -2.5$ selected in the present review) affects the calculation of $\log_{10} K^{\circ}_{s,0}$. Calculating the aqueous speciation with the hydrolysis constants and SIT coefficients selected in the present review, the solubility constant of $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.3)$ is obtained from the titration-LIBD data. The same value, but with an increased uncertainty ($\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$), is obtained from the solubility data determined at $pH_c = 3 - 4$ with an X-ray amorphous $ThO_2{\cdot}xH_2O$ ($x \approx 2.4$) dried for one week in a vacuum desiccator. This value is in agreement with $\log_{10} K^{\circ}_{s,0} = -(48.0 \pm 0.5)$ calculated by this review from solubility data of [1994OST/BRU] with a solid phase $ThO_2{\cdot}xH_2O$ ($x \approx 2.5$) prepared and dried with the same procedures, but considerably lower than the mean value of $\log_{10} K^{\circ}_{s,0} = -(46.7 \pm 0.9)$ selected in the present review for fresh amorphous precipitates not dried but only washed with water.

The solubility data measured at pH < 3 were not used for the evaluation of $\log_{10} K^{\circ}_{s,0}$, because they obviously refer to a more crystalline solid consisting of larger particles (*cf.* discussion in Section VII.4.3). The mean value of the thorium concentrations at pH > 10 (given with a 2σ uncertainty interval), $\log_{10}[Th] = -(8.2 \pm 0.9)$, is consistent with the value of $\log_{10}[\mathrm{Th(OH)_4(aq)}] = -(8.5 \pm 0.6)$ selected in [2001NEC/KIM] from literature data. However, due to possible problems arising from incomplete removal of colloids by centrifugation, Neck *et al.* [2002NEC/MUL] assumed that the concentration of mononuclear $\mathrm{Th(OH)_4(aq)}$ is more likely represented by the lower values at $\log_{10}[\mathrm{Th}] \approx -9$.

Figure A-44: Solubility data for $\mathrm{ThO_2}$(am, hyd) in 0.5 M NaCl [2002NEC/MUL]. Recalculation of the solubility constant and aqueous speciation using hydrolysis constants and SIT coefficients selected in the present review



In a separate section the authors describe EXAFS measurements in hydrolysed Th(IV) solutions and on the amorphous solid phase. Details of these measurements were published in [2002ROT/DEN]. The EXAFS data of the $\mathrm{Th^{4+}}$ ion in 1.5 M $\mathrm{HClO_4}$ are taken from a previous study [1999MOL/DEN]. The authors indicate that their observations support the selected speciation scheme. Their arguments can be questioned, since their solution B1 ($[\mathrm{Th}] = 5.0 \times 10^{-3}$ M, $-\log_{10}[\mathrm{H^+}] = 3.02$) contains 59% $\mathrm{Th^{4+}}$ and 31% $\mathrm{Th(OH)^{3+}}$, but the speciation is strongly dependent on the selected hydrolysis constants. By using the values selected in this review the fraction of $\mathrm{Th(OH)^{3+}}$ is lower and that of $\mathrm{Th_2(OH)_2^{6+}}$ is higher. It is well known that bond distances of $\mathrm{OH^-}$ and $\mathrm{F^-}$ to metal ions are very similar in the solid state. One would therefore expect the Th–$\mathrm{OH^-}$ distance to be close to that of Th–F$^-$, equal to 2.20 Å; if the test solution contained 31% of $Th(OH)^{3+}$ one should be able to detect this distance, as in [1999MOL/DEN]. The EXAFS spectra of samples B2, C2 and particularly sample C1 (at H^+ and Th concentrations exceeding the solubility limit, but in the stability range of colloids) are significantly different from that of Th^{4+} and sample B1. The presence of large amounts of polynuclear Th(IV) species or colloids with highly asymmetric Th–O coordination is indicated by a broad asymmetric Th–O FT peak, similar to that for the EXAFS spectrum of the amorphous oxyhydroxide solid $ThO_n(OH)_{4-2n}\cdot xH_2O(am)$.

[2002PER/RIG]

The authors report the solubility of $ThO_2\cdot xH_2O(am)$ in 1) 0.1 M $NaClO_4$ as a function of pH, 2) 0.001, 0.01, 0.08, and 0.14 M Na_2SiO_3 solutions at 25°C and at selected pH values ranging from 4 to 12, and 3) 0.08 and 0.14 M Na_2SiO_3 solutions at 90°C and at a few selected pH values ranging between 4 and 12. They report that their measured solubilities of $ThO_2\cdot xH_2O(am)$ in the absence of silica are similar to those previously reported in the literature, although their limiting solubilities ($10^{-10.4}$) at pH values >6 are lower than previously reported. They state that the observed aqueous thorium concentrations, ranging between 10^{-5} and 10^{-7} M at pH $6-12$ in the presence of silica, result from the formation of a thorium hydroxo-silicate compound.

No thermodynamic data are reported in this paper. No characterisation data, other than bulk analysis, are available for the so-called thorium hydroxo-silicate compound. Based on data reported in [2005MAZ/USH] and [2005RAI/YUI], no thorium silicate-based solids are expected to be precipitated, at least not at high pH values. At the high concentrations of silica ($>>0.01$ M) used in these experiments, it is expected that $SiO_2(am)$ will precipitate in the entire range of pH values investigated in this study. Therefore the solid observed in their study may be just a mixture of $ThO_2\cdot xH_2O(am)$ and $SiO_2(am)$ rather than a single solid phase as they propose. The Na_2SiO_3 reagent generally has significant carbonate impurities. The authors do not state whether they checked their solution for carbonate. The level of carbonate impurities generally present in Na_2SiO_3 is expected to affect significantly the thorium concentrations, especially in the relatively concentrated Na_2SiO_3 solutions and in the pH region around 8 and 9. Carbonate impurities are not expected to have an impact at higher pH values (*e.g.* 11 and 12). Therefore, there are large uncertainties in the reported data, especially for pH values below about 9 and in relatively concentrated silicate solutions (≥ 0.08 M) due to possible complexation of Th with carbonate. There is a large scatter in the thorium concentrations as a function of pH and at 0.08 and 0.14 M Na_2SiO_3 concentrations, the only data where the suspensions were filtered through low MW membrane filters, which is not conducive to any meaningful reinterpretation of this data. However, a general significant increase in thorium concentrations at high pH values (around 11 and 12) might indicate the possible existence of thorium complexes with polynuclear silica species.

[2002ROB/DAC]

The authors have studied the dissolution of thorium phosphate diphosphate (TPD) with and without trivalent actinides; they also studied a solid solution of Th(IV)/Pu(IV) phosphate diphosphate. The experiments consist of leaching studies where the rate of dissolution has been measured as a function of pH. This study does not provide any information on the solubility product of TPD. There is information on estimated equilibrium constants for $MPO_4(s)$ phases, where M = Am, Cm, Ce and Pr. These are secondary phases formed in the leach system.

[2002TOR/FAR]

The complexation of Th(IV) and various Ln(III) by glycolic acid ($HO\text{-}CH_2\text{-}COO^-$) has been investigated in 3.0 M $NaClO_4$ by potentiometry, ^{13}C-NMR spectroscopy and EXAFS. Glycolate may be bonded in two ways: either through the carboxyl group or by formation of a chelate. The formation of mononuclear complexes $Th(HO\text{-}CH_2\text{-}COO^-)_n$; $n = 1-4$, were identified in the $-\log_{10}[H^+]$ range 2.5 − 4.5 and the equilibrium constants of these complexes were determined using least squares refinement. The multinuclear complexes $Th_2(OH)_2(HO\text{-}CH_2\text{-}COO^-)_n$ were also established from potentiometric results and ^{13}C-NMR spectra.

The chelate-bonded complexes, $M_4(O\text{-}CH_2\text{-}COO^-)_n(OH\text{-}CH_2\text{-}COO^-)_{8-n}$; $n = 6$, 8 for Th(IV) and 6 − 8 for Ln(III), were identified in the higher $-\log_{10}[H^+]$ range. The structural model of these tetranuclear complexes having a tetranuclear core $M_4(O\text{-}CH_2\text{-}COO^-)_4$ with the triple-bridging was proposed from the information from ^{13}C-NMR spectroscopy and EXAFS. The EXAFS data give a Th–Th distance of 3.97 Å, with oxygen in the deprotonated OH-group as the bridging atom. The distance is close to that found in the polynuclear hydroxide system [1968JOH2]. The equilibrium constants proposed in this study refer to complexes with organic ligands and are therefore not included among the selected constants. However, the study demonstrates the role that ternary hydroxide complexes may play.

[2002YAN/TSU]

This paper of Yang *et al.* is discussed together with [2001YAN/TSU] from the same group of authors using quantum mechanical and molecular dynamical simulations to study the hydration sphere of Th^{4+}.

[2003AGA/PRA]

Enthalpy increments of $ThO_2(cr)$ were measured using a high temperature Calvet drop calorimeter from 376 to 940 K (20 measurements). The $ThO_2(cr)$, prepared by the oxalate route, contained less than 1000 ppm impurity, presumably including the 500 ppm MgO deliberately added as a sintering aid.

The results were fitted to an equation which leads to the heat capacity expression:

$$[C_{p,\mathrm{m}}]_{376\mathrm{K}}^{940\mathrm{K}}(\mathrm{ThO_2,cr},\ T) = 71.6726 + 8.2532\times10^{-3}\,T + 1.116094\times10^{6}\,T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

These data are very similar to the many other consistent measurements of the enthalpy increments of ThO_2(cr).

Similar measurements were made on four ThO_2-rich $Th_xU_{1-x}O_2$ compositions.

[2003BIT/MUL]

Bitea *et al.* [2003BIT/MUL] discuss the stability of thorium colloids generated by coulometric titration of 10^{-5} to 10^{-2} M thorium solutions at pH 3 − 5 in 0.5 M NaCl. Using laser-induced breakdown detection (LIBD) and ultrafiltration the colloids formed above the solubility limit of Th(IV) hydroxide were found to be stable within the time period of investigation (up to more than 400 days). Dilution of colloid containing test solutions at constant pH leads to the degradation of colloids into soluble ionic species, whereas dilution with neutral 0.5 M NaCl results in increased over-saturation and colloid formation, as recognised by a pH shift to lower values. This observation was ascribed to the simplified reaction:

$$\mathrm{Th(OH)}_n^{4-n} + (4{-}n)\,\mathrm{H_2O(l)} \rightleftharpoons \text{"Th(OH)}_4\text{(coll)"} + (4{-}n)\,\mathrm{H^+} \qquad \text{(A.112)}$$

Finally pH, ionic thorium species and colloids were found to approach a steady state which is comparable to the solid-liquid equilibrium of amorphous Th(IV) hydroxide determined in [2002NEC/MUL] with the coulometric titration-LIBD method.

[2003HEL/NAV]

The enthalpies of formation of three brannerite compositions, namely, $CeTi_2O_6$(cr), $U_{0.97}Ti_{2.03}O_6$(cr), and $ThTi_2O_6$(cr), have been measured by high temperature drop calorimetry at 976 K, using a solvent with the composition $3Na_2O\cdot4MoO_3$. The interest in these compounds is related to the potential of titanate-based ceramics for the immobilisation of actinides. The calorimetric procedure is described and the calorimeter is calibrated using the heat content of α-Al_2O_3. Drop solution enthalpic effects were measured by dropping pellets (about 5 mg) of the powdered samples from room temperature (presumably 25°C) into the solvent at the calorimeter temperature. Solution enthalpies were measured after equilibration of sample pellets above the solvent at the calorimeter temperature. In this way, the heat content increments could be taken in account.

The brannerite samples were prepared by sintering ball-mixed stoichiometric amounts of the oxides, namely, for the thorium compound, ThO_2(cr) and TiO_2(anatase) in air at 1773 K for more than 100 hours. X-ray powder diffraction of the compounds showed that they are monoclinic, belonging to space group *C*2/*m*. The lattice parameters reported for the thorium compound $ThTi_2O_8$ were a = (9.8046 ± 0.0008) Å, b = (3.8187 ± 0.0003) Å, c = (7.0229 ± 0.0005) Å, and β = (118.852 ± 0.005)°, giving, as expected, a slightly larger cell volume than that obtained for the corresponding uranium compound. Quantitative analysis by the Rietveld method indicated a sample composition of (0.991 ± 0.003) weight fraction $ThTi_2O_6$ and (0.009 ± 0.001) weight fraction

ThO_2 These results were confirmed by back-scattered electron images which gave 0.9902 weight fraction $ThTi_2O_6$ and 0.0098 weight fraction ThO_2. Electron microprobe analysis with wavelength dispersion spectroscopy indicated that the thorium and titanium contents were, within the uncertainties, equal to stoichiometric values. After correction for the small thorium dioxide impurity, a value of (19.4 ± 1.6) $\text{kJ}\cdot\text{mol}^{-1}$ was reported for Reaction (A.113) corresponding to the enthalpy of the formation reaction of thorium brannerite from the binary oxides,

$$ThO_2(\text{cr, 298.15 K}) + 2TiO_2(\text{rutile, 298.15 K}) \rightarrow ThTi_2O_6(\text{cr, 298.15 K}) \qquad \text{(A.113)}$$

This result indicates that Th-brannerite is entropy-stabilised and may be stable at high temperature only.

Taking this value, with slightly increased uncertainty limits, namely, (19.4 ± 2.0) $\text{kJ}\cdot\text{mol}^{-1}$ and making use of the values selected in this review for $\Delta_f H^\circ_m$ (ThO_2, cr, 298.15 K) = – (1226.4 ± 3.5) $\text{kJ}\cdot\text{mol}^{-1}$ and (TiO_2, rutile, 298.15 K) = – (944.0 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$ yields the value:

$$\Delta_f H^\circ_m (ThTi_2O_6, \text{cr, 298.15 K}) = -(3095.0 \pm 4.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

The authors report also values of (29.6 ± 3.6) $\text{kJ}\cdot\text{mol}^{-1}$ and $-(7.7 \pm 2.8)$ $\text{kJ}\cdot\text{mol}^{-1}$, respectively, for the enthalpies of the formation reaction of $CeTi_2O_6$(cr) and $U_{0.97}Ti_{2.03}O_6$(cr) from the binary oxides.

Thus the results indicate that both the thorium and the cerium titanates are entropy stabilised compounds and are probably stable at high temperature only, while uranium titanate is presumably stable at ambient conditions.

[2003NEC/ALT]

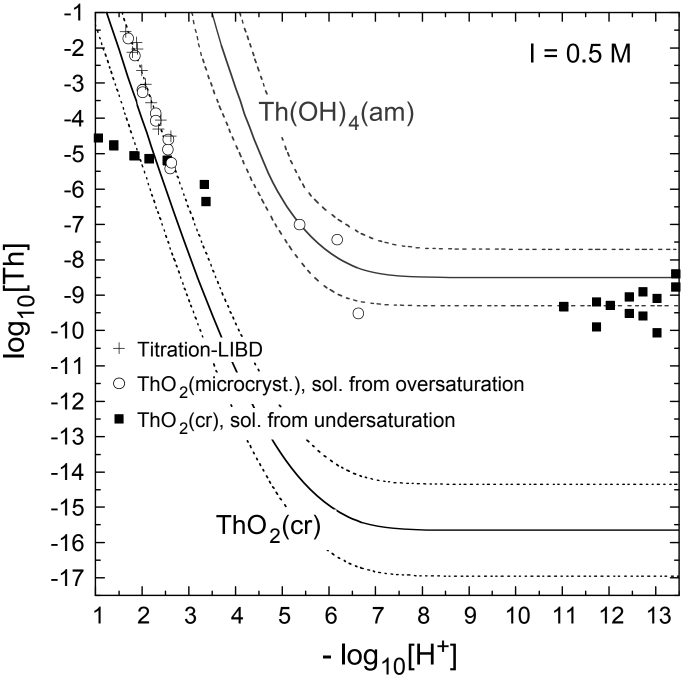
This review concerns the two related papers by [2000BUN/KNO] and [2003NEC/ALT] on the formation of colloids in the precipitation of microcrystalline ThO_2(s, hyd). In the first study, Bundschuh *et al.* [2000BUN/KNO] have used coulometric titration in combination with the LIBD (Laser Induced Breakdown Detection) method to detect the onset of colloid formation and also to estimate the number of particles formed and their average size. The data have been obtained at 25°C in 0.50 M NaCl, where the colloid formation has been measured as a function of $-\log_{10}[H^+]$ at total thorium concentrations varying between 9×10^{-5} and 2.9×10^{-2} M. The $-\log_{10}[H^+]$ range varied between 1.6 and 2.6. It turns out that ThO_2 colloids are formed at low pH, well before precipitation can be observed experimentally. The detection of the point where colloids are formed also indicates the point where equilibrium between solid and solution is attained. The calculated solubility product, $\log_{10} K_{s,0} = -(49.54 \pm 0.23)$ at the 2σ-level, was recalculated to zero ionic strength using the SIT: $\log_{10} K^\circ_{s,0} = -(52.8 \pm 0.3)$. This value refers to a colloidal hydrous oxide with a particle size in the range of 16 to 23 nm [2000BUN/KNO].

The same titration-LIBD method and equipment is used in a second study of this group [2003NEC/ALT] to confirm the reproducibility of these results by three additional titration experiments at thorium concentrations of 7.6×10^{-3}, 5.0×10^{-5} and 3.2×10^{-5} M. The mean value of the solubility product calculated from the data determined in both studies is found to be $\log_{10} K_{s,0} = -(49.6 \pm 0.5)$ (2σ) in 0.5 M NaCl and $\log_{10} K^{\circ}_{s,0} = -(52.9 \pm 0.5)$ at zero ionic strength. In addition, the formation of visible precipitates was observed after storing the colloidal ThO_2 suspensions produced in the titration-LIBD experiments of [2000BUN/KNO] and [2003NEC/ALT]. The microcrystalline nature of these ThO_2(cr, hyd) precipitates obtained at pH 1.5−2.5 was confirmed by EXAFS and XRD analyses. The H^+ and Th concentrations were measured 19−160 days after precipitation; they decrease with a slope of −4 in a logarithmic solubility plot, indicating that these solubility data determined from the direction of oversaturation actually refer to the equilibrium between microcrystalline ThO_2(cr, hyd) and Th^{4+}. The corresponding solubility product of $\log_{10} K_{s,0} = -(49.9 \pm 0.4)$ in 0.5 M NaCl and $\log_{10} K^{\circ}_{s,0} = -(53.2 \pm 0.4)$ (uncertainties given as 2σ) is somewhat lower than the value obtained by the titration-LIBD method. Using the equations of Schindler [1967SCH], the solubility product for a crystalline phase with large particle size is estimated to be 1.0 to 1.4 logarithmic units lower. Accordingly, the experimental solubility constants of $\log_{10} K^{\circ}_{s,0}$ (particle size d = 16−23 nm) = −52.8 to −53.2 are in reasonable agreement with the value calculated from thermochemical data for crystalline ThO_2(cr), $\log_{10} K^{\circ}_{s,0} = -(54.2 \pm 1.3)$.

The findings of [2000BUN/KNO], [2003NEC/ALT] are important for solubility measurements because colloids result in a measured solubility that is too large, if the colloidal fraction cannot be removed prior to the thorium analysis (this is usually done using filtration or ultracentrifugation). However, the conclusion of [2000BUN/KNO] who assumed that the much higher solubility data reported in the literature for amorphous Th(IV) hydroxide or hydrous oxide must be affected by inclusion of colloids, is not correct. It is certainly possible to prepare colloid-free thorium solutions at higher pH and thorium concentrations as observed in a later study of these authors [2002NEC/MUL]. The observed formation of microcrystalline ThO_2 colloids at pH < 2.5 has no implications for the analysis of potentiometric data at pH > 2.5.

The second study [2003NEC/ALT] also includes a solubility study with commercially obtained anhydrous ThO_2(cr). The study was performed from undersaturation in 0.1 and 0.5 M HCl-NaCl solutions and in 0.5 M NaOH-NaCl solutions ($-\log_{10} [H^+]$ = 11.0−13.5). However, as in an analogous study of [2001HUB/BAR], the thorium concentrations measured in acidic solutions after 79−318 days were not equilibrium values. The values of $\log_{10}$ [Th] in the range of $-\log_{10} [H^+]$ = 1.0−2.5 show only a slight pH-dependence, whereas equilibrium values of $\log_{10} [Th^{4+}]$ are expected to decrease with a slope of −4. The thorium concentration at pH 1 is several orders of magnitude lower than the calculated equilibrium value (*cf.* Figure A-45).

Figure A-45: Experimental data determined in [2000BUN/KNO], [2003NEC/ALT] for ThO_2 colloids using the titration-LIBD method. The solubility from oversaturation after precipitation of microcrystalline ThO_2(cr, hyd) and from undersaturation with crystalline ThO_2(cr) are compared to the solubility curves calculated for ThO_2(cr) and $Th(OH)_4$(am) (from [2003NEC/ALT]).



The thorium concentrations measured in [2003NEC/ALT] with crystalline ThO_2(cr) after 71 and 122 days in the alkaline range are orders of magnitude higher than the value of $\log_{10}[Th(OH)_4(aq)] = -(15.6 \pm 1.3)$ expected for the reaction:

$$ThO_2(cr) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq) \qquad (A.114)$$

from the solubility constant $\log_{10}{}^*K^\circ_{s,0}$ (ThO_2, cr, 298.15 K) = (1.8 ± 1.1) and $\log_{10}{}^*\beta^\circ_{4,1} = -(17.4 \pm 0.7)$ selected by this review. The mean value, $\log_{10}[Th] = -(9.3 \pm 0.8)$ (given with an uncertainty of $\pm 2\sigma$), is close to the solubility of $Th(OH)_4$(am) (*cf.* Figure A-45). Similar values for crystalline ThO_2(cr) in neutral and alkaline solution were reported in [1989MOO], [1998WIE/HEL] [2000FOU/VIN] [2001HUB/BAR]. These experimental findings may be caused by small amounts of amorphous fractions of the otherwise crystalline solid. Neck *et al.* [2001NEC/KIM], [2002FAN/NEC], [2003NEC/ALT] assumed that the slow dissolution of ThO_2(cr) followed by the very fast hydrolysis reactions of the Th^{4+} ions might result in an irreversible dissolution reaction. They suggest that the back-reaction, *i.e.*, the sorption or precipitation of monomeric or polynuclear hydroxide complexes $\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$ on the surface of crystalline ThO_2(cr), would lead to an amorphous, solubility controlling surface layer of "$Th(OH)_4$(am)".

[2003OKA/MOC]

This is a theoretical study using *ab initio* quantum mechanics in combination with a polarisable continuum model (PCM) for the solvent. The theoretical approach is satisfactory both for the determination of structures and energetic in the ground and transition states; the latter refer to the transfer of a proton from water coordinated in the first, to water in the second coordination sphere. The reactions studied are:

$$\mathrm{Th(H_2O)}_N^{4+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)(H_2O)}_{N-1}^{3+} + \mathrm{H_3O^+}$$

$$\mathrm{Th(OH)(H_2O)}_{N-1}^{3+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)_2(H_2O)}_{N-2}^{2+} + \mathrm{H_3O^+}$$

$$\mathrm{Th(OH)_2(H_2O)}_{N-2}^{2+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)_3(H_2O)}_{N-3}^{+} + \mathrm{H_3O^+}$$

where $N = 1-4$ for the first reaction and $N = 4$ for the second and third reaction. As the coordination number of Th^{4+} is $9-11$ according to the previous theoretical [2001YAN/TSU], [2002YAN/TSU] and experimental studies [1968JOH2], [1999MOL/DEN], it is clear that the chemical model is not appropriate to describe experimental data. The authors are aware of this and note that they were not able to study the transition state of systems with larger coordination numbers; this review suggests that it should be feasible to study the thermodynamics of the reactions. In view of shortcomings of the chemical model the calculated reaction energies are not in good agreement with experimental data.

[2003SAW/SHA]

The hydrolytic behaviour of thorium(IV) and dioxo-uranium(VI) was studied using potentiometric determinations of the hydrogen ion concentration at 25°C in 1.0 M $NaClO_4$; only the thorium data will be discussed here. Seven different titrations with total concentrations of thorium(IV), $[\mathrm{Th}]_{\mathrm{tot}}$ = 0.045, 0.214, 1.05, 1.07, 1.09, 1.14, and 1.09 mM were made; in one of them a small amount of fluoride, about 1% of $[\mathrm{Th}]_{\mathrm{tot}}$ was added. The pH range studied in the different titrations varied but the overall variation was from 1.5 to 5.1. The titrations were made by adding successive amounts of a NaOH solution to test solutions with the initial concentrations given above. Hence the total concentration varied throughout the titration. The authors report pH values but they determined the E° value of the glass electrode using the Gran method. The methodology was tested by determination of the dissociation constant of acetic acid and $\mathrm{p}K_{\mathrm{w}}$ of water. Titration with NaOH is not the best experimental approach due to the risk of local precipitation when the titrant is added; it is then important to ensure that equilibrium has been attained and it seems to this review that a longer equilibration time than one minute, used in most titrations, is necessary. The authors also note that a titration where the equilibration time was 10 minutes had to be rejected because these data could not be refined using their least-squares approach. This suggests that equilibrium might not have been attained after one minute. The experimental data were refined using HYPERQUAD where the program fitted each experimental titration curve by a certain chemical model, in this case the equilibrium constants for two complexes $Th(OH)^{3+}$ and $Th(OH)_3^+$. The average values are $\log_{10}{}^*\beta_{1,1} = -(3.51 \pm 0.03)$ and $\log_{10}{}^*\beta_{3,1} = -(10.75 \pm 0.14)$. From a scrutiny of Figure 6 in [2003SAW/SHA] it is obvious that this model does not fit the experimental titration curve very well; unfortunately the authors have not stated to which experiment this curve belongs. At first sight, the fit seems good because of the large scale used, but closer scrutiny reveals noticeable and systematic discrepancies, in particular at low pH.

There is strong evidence from other investigations discussed in the present review that polynuclear thorium complexes are formed in the $[Th]_{tot}$-pH range investigated, complexes that have not been found by Sawant *et al.* This review considers this as an indication of unidentified errors in [2003SAW/SHA] and does therefore not accept the equilibrium constants proposed.

The authors have also made titrations where a small amount of fluoride was added to the test solutions; the rationale for this is not clear and the suggestion that fluoride addition should result in the prevention of colloid formation is not quantified.

[2003TOR/GRE]

The complex formation in the binary Th(IV)-5-sulphosalicylate (SSA^{3-}) system and in the corresponding ternary fluoride system was investigated using potentiometry and proton and fluorine NMR spectroscopy. The equilibrium constants for the reactions

$$p\,\mathrm{Th}^{4+} + r\,\mathrm{SSA}^{3-} \rightleftharpoons \mathrm{Th}_p\mathrm{H}_{-q}(\mathrm{SSA})_r^{4p-q-3r} + q\,\mathrm{H}^+$$

were determined at 25°C in an ionic medium with constant concentration of Na^+ equal to 1.00 M. Three mononuclear complexes $Th(HSSA)^{2+}$, $Th(SSA)^+$ and $Th(SSA)_2^{2-}$, were identified in the $-\log_{10}[H^+]$ range 1.7−3.5. The NMR data indicate that the SSA ligand in $Th(HSSA)^{2+}$ is only coordinated *via* the carboxylate group, *i.e.* the aromatic OH-group is not deprotonated. In the other two complexes the OH-group is deprotonated, resulting in the formation of very stable chelate complexes. Two additional fluoride ions can coordinate to $Th(SSA)^+$ and $Th(SSA)_2^{2-}$, even at low total concentrations of fluoride. At $-\log_{10}[H^+] > 3.5$ bi- and tetranuclear complexes, $Th_2(OH)_2(SSA)_4^{6-}$ and $Th_4(OH)_4(SSA)_{10}^{18-}$, were identified by using a combination of potentiometry and NMR data. The binuclear complex can bind three additional fluoride ions, indicating nine-fold coordination around the Th, where the thorium ions are linked with a double hydroxide bridge. The complex $Th_4(OH)_4(SSA)_{10}^{18-}$ cannot bind additional fluoride ions, indicating that Th is eight coordinated. From the stoichiometry of the complex and the NMR data the authors conclude that the complex contains a cubane-like "$Th_4(OH)_4$" core, similar to the ones suggested in binary hydroxide systems [1969BAC/BRO].

A comparison of the data presented in [2002TOR/FAR] and [2003TOR/GRE] shows that much stronger complexes are formed with organic ligands containing aromatic OH-groups (like 5-sulphosalicylate) than those containing aliphatic ones (like glycolate). This observation is important when modelling the complex formation between actinides and humic and fulvic acids.

Toraishi and Grenthe [2003TOR/GRE] provide information that the formation of polynuclear Th(IV) complexes is not restricted to the binary Th(IV)-hydroxide system. They also show that fluoride binds strongly to Th(IV) even in the presence of other ligands. These are chemical aspects that need to be considered when modelling the speciation of Th(IV) in aquatic systems. As the present review does not include organic ligands the equilibrium constants determined in [2003TOR/GRE] are not listed.

[2003YAN/TSU]

This paper is discussed together with [2003TSU/YAN].

Both these studies discuss the structure and coordination number of the Th(IV) aquo ion, $\mathrm{Th(OH_2)}_n^{4+}$ by the use of quantum chemical methods, where the solvent has been described by using a continuum model. In this, the solvent is described as a conductor-like polarisable continuum with the same dielectric constant as water. Standard quantum chemical methods have been used with the core electrons replaced by effective relativistic core-potentials. The structure and relative energy of aquo ions with different coordination number and coordination geometry have been compared. Calculated $\mathrm{Th^{4+}}$-$\mathrm{OH_2}$ bond distances are in fair agreement with experimental data. The calculations indicate that the $\mathrm{Th^{4+}}$ aquo ion has the stoichiometry $\mathrm{Th(OH_2)_9^{4+}}$ with D_{3h} symmetry as judged by a comparison of the relative energy of $[\mathrm{Th(OH_2)_9^{4+}}]$ and $[\mathrm{Th(OH_2)_8^{4+}}],(\mathrm{H_2O})$, where the latter complex with one water in the second coordination sphere has the higher electronic energy. A similar comparison between $[\mathrm{Th(OH_2)_{10}^{4+}}]$ and $[\mathrm{Th(OH_2)_9^{4+}}],(\mathrm{H_2O})$ shows that the first complex is marginally more stable, by *ca.* 1 kJ·mol^{-1}, far less than the uncertainty in this type of calculations. A comparison between $[\mathrm{Th(OH_2)_9^{4+}}],(\mathrm{H_2O})_3$ and $[\mathrm{Th(OH_2)_{10}^{4+}}],(\mathrm{H_2O})_2$ shows that the latter is less stable by 7 kJ·mol^{-1}. Comparisons of the relative energy of the different complexes should be made by using the difference in Gibbs energy, rather than the electronic energy. However, this is often not possible because of the high computational cost for the estimate of vibration energy levels required for the molecular partition functions. The energy difference between eight- and nine-coordinated aquo-ions is sufficiently large to conclude that the nine-coordinated species is the more stable one. The difference between nine and ten-coordination is so small that it is difficult to decide on their relative stability, the two species might even be in equilibrium in solution as found among the trivalent lanthanide aquo-ions. In the second study, [2003YAN/TSU], there is also a discussion of the mechanism for the exchange of water between the first and second coordination spheres of Th(IV). The authors have also discussed the structure and rate of water exchange in $[\mathrm{Th(OH)(OH_2)_8}]^{3+}$. Both studies provide information on the chemical properties of the Th(IV) aquo ion but no thermodynamic data. These studies contain essentially the same information as in [2001YAN/TSU] and [2002YAN/TSU].

[2004ALT/NEC]

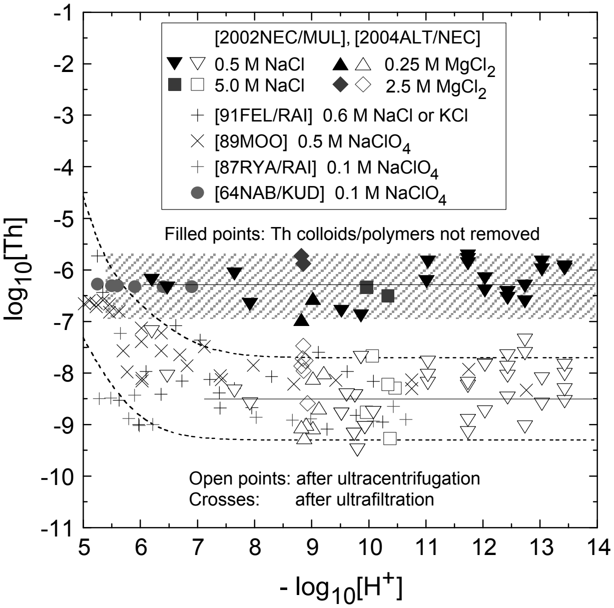
Altmaier *et al.* [2004ALT/NEC] describe the solubility of crystalline ThO_2(cr) and amorphous Th(IV) oxyhydroxide and the colloid formation (determined from the Th concentration in the supernatant and after ultracentrifugation) in concentrated NaCl and $MgCl_2$ solutions (brines) at (22 ± 2)°C. These solutions are models for the brines present in rock salt formations. The solubility increasing effect of long-time stable Th(IV) colloids previously studied in 0.5 M NaCl solutions [2002NEC/MUL] is observed also in 5 M NaCl, 0.25 M $MgCl_2$ and 2.5 M $MgCl_2$. The ionic strength has no influence on the stability of these colloids. The solubility increasing effect of Th(IV) eigencolloids is fairly large at $pH > 7$ and corresponds to a total concentration of $[\mathrm{Th}]_{\mathrm{tot}} \approx [\mathrm{Th}]_{\mathrm{coll}} = 10^{-6.3 \pm 0.5}$ M, which was ascribed to the equilibrium reaction:

$$\mathrm{Th(OH)_4(am)} \rightleftharpoons \mathrm{Th(OH)_4(coll)} = 1/m\ \mathrm{Th}_m\mathrm{(OH)}_{4m}\mathrm{(aq)} \qquad \text{(A.115)}$$

In 4.5 M $MgCl_2$ solutions saturated with $Mg_2(OH)_3Cl$(s), magnesium oxychloride colloids are formed that sorb Th(IV) species strongly, resulting in an increase of the total thorium concentration to 10^{-5} M. These findings are discussed with regard to geochemical modelling of colloidal Th(IV) and Pu(IV) concentrations.

The total thorium concentrations observed in both over- and undersaturation experiments with amorphous Th(IV) precipitates were analysed by ultracentrifugation which showed that the removal of Th(IV) eigencolloids requires a large centrifugal force of about 1.5×10^5 g (rotation velocities of 50000 rpm). Increasing the rotation velocity to about 5×10^5 g (90000 rpm) did not lead to a further decrease of the thorium concentration, indicating that the thorium remaining dissolved is present as small aqueous species. As shown in Figure A-46, the thorium concentration measured by Nabivanets and Kudritskaya [1964NAB/KUD] at pH 6−7 after centrifugation at 10000 rpm, $\log_{10}[\mathrm{Th}] = -6.3$ is equal to that determined by [2002NEC/MUL], [2004ALT/NEC] in the supernatant solutions without removing polymeric or colloidal species. The centrifugal force used by [1964NAB/KUD] is not sufficient to remove small Th(IV) polymers or colloids. This reproducible Th concentration is two orders of magnitude higher than those determined at pH 6 to 14 after ultrafiltration (pore size 1.3−2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI] or ultracentrifugation at 5×10^5 g [2002NEC/MUL], [2004ALT/NEC] and obviously not caused by $Th(OH)_4$(aq) but by polymeric species $\mathrm{Th}_m\mathrm{(OH)}_{4m}$(aq) in the range 1.5−2 nm.

Figure A-46: The pH-independent thorium concentrations determined in neutral to alkaline solutions at 17 to 25°C. Filled points (hatched area): Thorium colloids/polymers not removed [2002NEC/MUL], [2004ALT/NEC], [1964NAB/KUD]. Open points: Data measured after ultracentrifugation for one hour at at 5×10^5 g [2002NEC/MUL], [2004ALT/NEC]. Crosses: Data measured after ultrafiltration (pore size 1.3 – 2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI].



[2004BEN/BOU]

This study has been made using potentiometry, the measurement of pH at 25°C, in a 0.1 M $NaClO_4$ ionic medium; the pH range 3.82 – 9.73 was investigated. The test solution had a total thorium concentration of 0.10 mM and it was titrated with 0.1 M or 1.0 M NaOH. It is obvious that no reliable data can be obtained under these conditions, *i.e.*, at Th concentrations up to 4 orders of magnitude above the solubility of ThO_2(am, hyd). Nevertheless, the authors have used their experimental data in a least-squares program that suggested that the following species are formed: $Th(OH)_2^{2+}$, $Th(OH)_3^+$, $Th(OH)_4$(aq) and $Th_2(OH)_7^+$ with the equilibrium constants, $\log_{10} {}^*\beta_{2,1}(Th(OH)_2^{2+}) = -(8.36 \pm 0.11)$, $\log_{10} {}^*\beta_{3,1}(Th(OH)_3^+) = -(11.63 \pm 0.09)$, $\log_{10} {}^*\beta_{4,1}$ ($Th(OH)_4$, aq) $= -(18.24 \pm 0.13)$ and $\log_{10} {}^*\beta_{7,2}(Th_2(OH)_7^+) = -(24.32 \pm 0.08)$. The authors do not report any test of alternative chemical models and there is no comparison between experimental and calculated titration curve.

The literature survey provided is very incomplete and most of the important previous studies are not mentioned, including the monograph of Baes and Mesmer [1976BAE/MES]. The introduction of the paper gives strong evidence that the authors are not familiar with solution and coordination chemistry. The data given in [2004BEN/BOU] are not useful.

[2004HEI/HUB]

Heisbourg *et al.* [2004HEI/HUB] prepared mixed Th(IV)-U(IV) oxides, $Th_{1-x}U_xO_2(cr)$ with $x = 0.24, 0.37, 0.53, 0.67$, and 0.81, and investigated their dissolution behaviour under oxidising conditions at room temperature in 0.1 M HNO_3-KNO_3 ($-\log_{10}[H^+] = 1$, 2, 3, and 4) and in 1 and 5 M HNO_3. The results were presumably obtained at 20−25°C. The solids were investigated by XRD, particle induced X-ray emission analysis (PIXE) and electron probe micro analysis (EPMA). X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used to determine the oxidation state of uranium. The dissolution behaviour was studied up to 800 days and the aqueous thorium and uranium concentrations were determined by ICP-MS after phase separation by centrifugation at 13000 rpm.

The dissolution rates observed for low and high fractions of thorium are discussed in comparison with those of pure $ThO_2(cr)$ and $UO_2(cr)$ and a possible mechanism is proposed including dissolution kinetics and kinetics of uranium oxidation. The authors observed enrichment of thorium in the mixed oxides and assumed that a protective surface layer of hydrated thorium oxide is formed as secondary phase. Heisbourg *et al.* [2004HEI/HUB] used the steady state thorium concentrations in 0.1 M HNO_3-KNO_3 reached after 100 days to calculate the solubility products of the $ThO_2(s)$ secondary phase. The $\log_{10} K^\circ_{s,0}$ values extrapolated to $I = 0$ (Table A-82) are in the range of experimental values for crystalline or microcrystalline thorium dioxide: $\log_{10} K^\circ_{s,0} \geq -55.0$ [2000RAI/MOO] and $\log_{10} K^\circ_{s,0} = -(53.2 \pm 0.4)$ [2003NEC/ALT] (extrapolated to $I = 0$ with the SIT). However, the calculated $\log_{10} K^\circ_{s,0}$ values in Table A-82 evidently increase with pH, and the values calculated from the data in 0.1 M HNO_3 are even lower than $\log_{10} K^\circ_{s,0}$ (ThO_2, cr) $= -(54.2 \pm 1.1)$ calculated from thermochemical data selected in the present review. This indicates either a certain stabilisation of thorium oxide in the solid solutions $Th_{1-x}U_xO_2(cr)$ or, similarly as in the dissolution studies with $ThO_2(cr)$ [2001HUB/BAR], that the thorium concentrations do not represent equilibrium values.

Table A-82: Solubility products $\log_{10} K^\circ_{s,0}$ (ThO_2 secondary phase) calculated in [2004HEI/HUB] from the dissolution experiments with $Th_{1-x}U_xO_2(cr)$ at $I = 0.1$ M (HNO_3-KNO_3).

	$-\log_{10}[H^+] = 1$	$-\log_{10}[H^+] = 2$	$-\log_{10}[H^+] = 3$	$-\log_{10}[H^+] = 4$
$Th_{0.76}U_{0.24}O_2(cr)$				$-(51.2 \pm 0.2)$
$Th_{0.33}U_{0.67}O_2(cr)$	$-(56.3 \pm 0.2)$	$-(53.3 \pm 0.2)$	$-(51.4 \pm 0.2)$	
$Th_{0.19}U_{0.81}O_2(cr)$	$-(56.2 \pm 0.2)$	$-(53.3 \pm 0.2)$	$-(51.9 \pm 0.2)$	

[2004KON]

The heat capacity data of the actinide(IV) oxides, fluorides and chlorides have been analysed, and the data expressed as the sum of three contributions: from the lattice vibrations, from *f*-electron excitation and from a residual term, probably arising from the interaction of *d*-electrons. It is demonstrated that the latter contribution becomes zero around $T = 500$ to 600 K. A similar approach is given for the entropies, from which the standard entropies of a number of An(IV) compounds have been estimated.

These estimates have been used in selecting the data at 298.15 K for β-$ThCl_4$. Unfortunately, this paper does not include estimates for the bromide and iodide, but such values are included in the later overview by Konings *et al.* [2006KON/MOR], and these have been selected by this review.

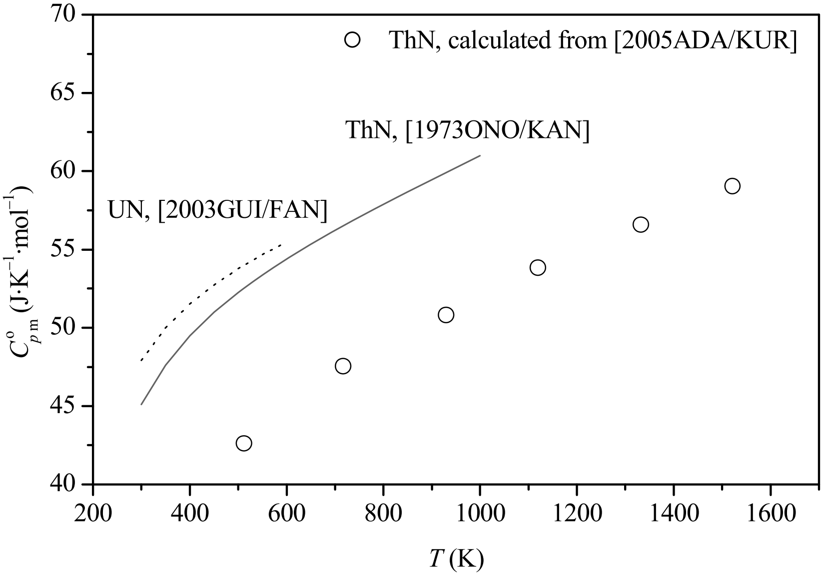
[2005ADA/KUR]

A molecular dynamics calculation was performed for thorium mononitride ThN(cr) in the temperature range from 300 to 2800 K to evaluate the thermophysical properties, *viz.* the lattice parameter, linear thermal expansion coefficient, compressibility, heat capacity ($C^{\circ}_{\mathrm{v,m}}$), and thermal conductivity. A Morse-type function added to the Busing-Ida type potential was employed as the potential function for interatomic interactions. The interatomic potential parameters were semi-empirically determined by fitting to the experimental variation of the lattice parameter with temperature.

For the heat capacity, only the lattice vibration and dilatational contributions could be evaluated from the molecular dynamics calculations. An electronic contribution of $C_{\mathrm{el}}(T) = 3.12 \times 10^{-3}\, T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) was added, based on the very low temperature results of de Novion and Costa [1970NOV/COS].

Figure A-47 shows a comparison of the authors' calculated values (presented only graphically in the paper) with the experimental values for $C^{\circ}_{p,\mathrm{m}}$ (ThN,cr) by [1973ONO/KAN], and also the assessed values for UN(cr) from [2003GUI/FAN]. It seems that the authors' predicted values of the total heat capacity are too low by *ca.* 10 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, perhaps due to an underestimation of the electronic contribution.

Figure A-47: Heat capacity of ThN(cr).



[2005ALT/NEC]

This is a careful experimental study of the solubility of ThO_2(am, hyd) and the complex formation in the ternary Th(IV)-hydroxide-carbonate system and an equally careful analysis and discussion of some previous publications, [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], and [1999FEL/RAI]. Altmaier *et al.* [2005ALT/NEC] have performed solubility studies with a $ThO_2{\cdot}xH_2O$(am) phase described in [2002NEC/MUL], very similar to that used by [1994OST/BRU], at 22°C and constant ionic strength of $I = 0.5$ M (NaCl media) under CO_2(g) partial pressures of 0.1 and 1.0 bar and in carbonate/bicarbonate buffers, partly with additions of NaOH. A few additional solubility measurements at high pH and carbonate concentrations are consistent with the results reported by Rai *et al.* [1995RAI/FEL]. The experimental procedures are described in detail. The equilibrium constants used to calculate the concentration of OH^-, HCO_3^- and CO_3^{2-} from the measured H^+ concentration were taken from the NEA-TDB review [2003GUI/FAN] and the unknown ion interaction coefficients $\varepsilon(Na^+, Th(OH)_y(CO_3)_z^{4-y-2z})$ were estimated (from known values for actinide complexes of analogous charge and similar size) to be: 0.1, 0.05, 0, −0.05, − 0.1, −0.15. − 0.2, −0.25 and −0.3 kg·mol^{-1} for Th(IV) complexes of charge +2, +1, 0, −1, −2, −3, −4, –5 and −6, respectively (estimated uncertainty: ± 0.2 kg·mol^{-1}).

The conclusions drawn in [2005ALT/NEC] are accepted by this review, based on the arguments in Section XI.1.3.2. The choice of equilibrium constants is justified due to the close agreement between the experimental solubility data and the solubilities calculated using the selected speciation model, *cf.* Figures XI.2 – XI.4. Additional comparison between experimental data and model calculations are given in Figure A-48 to Figure A-51. The equilibrium constants reported in [2005ALT/NEC] and those selected in the present value are listed in Table A-83.

Figure A-48 to Figure A-50 show the comparison between model calculations and experimental data from Altmaier *et al.* [2005ALT/NEC] under various conditions at $I = 0.5$ M, under $CO_2(g)$ ($p_{CO_2} = 0.1$ and 1.0 bar, $-\log_{10}[H^+] = 4.4 - 7.6$) and in carbonate/bicarbonate buffers ($C_{tot} = 0.10$, 0.04 and 0.015 M, $-\log_{10}[H^+] = 8.7 - 13.0$) and from [2006ALT/NEC] at $I = 0.1 - 4.0$ M and $C_{tot} = 0.02$ M and 0.10 M). Figure A-49 includes further comparable experimental data from [1994OST/BRU] and [1995RAI/FEL]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review, including the pentacarbonate complex $Th(CO_3)_5^{6-}$ which is not included in the speciation model of Altmaier *et al.*

Figure A-48 to Figure A-51 also show the contributions of the various complexes to the measured solubility. It is obvious that the relative contributions of the various complexes vary strongly with the experimental conditions. The species $Th(OH)(CO_3)_4^{5-}$ (114), $Th(OH)_2(CO_3)_2^{2-}$ (122) and $Th(OH)_4(CO_3)^{2-}$ (141) contribute significantly to the measured solubility in most of the experiments; these equilibrium constants are therefore accepted by this review. The contributions of the species $Th(OH)_2(CO_3)(aq)$ (121) and $Th(OH)_3(CO_3)^-$ (131) are limited to only a few experimental conditions where they amount to less than 50% of the total thorium concentrations; these equilibrium constants are therefore not selected but only recommended as guidance. The upper limits given in Table A-83 for numerous other complexes should not be used even in scoping calculations. These species give no contributions to the thorium concentrations in [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], [2005ALT/NEC] and [2006ALT/NEC]. If these species exist under other conditions (not covered in these studies), their equilibrium constants could be orders of magnitude lower than the reported upper limits. The stoichiometry and structure of the complexes formed in the ternary $Th(IV)$-OH^--CO_3^{2-} system are still not completely known. However the set of equilibrium constants proposed by [2005ALT/NEC] is in the judgment of this review the best available.

Table A-83: Equilibrium constants $\log_{10} K_{s,1yz}$ and $\log_{10} \beta_{1yz}$ and upper limits calculated in [2005ALT/NEC] for the formation of (1*yz*) complexes $\mathrm{Th(OH)}_y(\mathrm{CO}_3)_z^{4-y-2z}$ at $I = 0.5$ M and $I = 0$ (25°C). The equilibrium constants (uncertainties ± 2σ) refer to:

$$\mathrm{Th(OH)_4(am)} + z\,\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO}_3)_z^{4-y-2z} + (4-y)\,\mathrm{OH}^- \qquad \log_{10} K_{s,1yz}$$

$$\mathrm{Th}^{4+} + y\,\mathrm{OH}^- + z\,\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO}_3)_z^{4-y-2z} \qquad \log_{10} \beta_{1yz}$$

Complex	$\log_{10} K_{s,1yz}$	$\log_{10} K^{\circ}_{s,1yz}$ ($I = 0.5$ M)	$\log_{10} \beta^{\circ}_{1yz}$	$\log_{10} \beta^{\circ}_{1yz}$ This review
Hydroxide complexes				
(110)			11.8 ± 0.2 [a]	11.5 ± 0.5
(120)			21.4 ± 0.2 [a]	21.8 ± 0.5
(130)			30.6 ± 1.0 [a]	
(140)			39.0 ± 0.5 [a]	38.6 ± 0.7
Carbonate complexes				
(101)	< – 35.3	< – 35.8	< 12.0 [b]	
(102)	< – 27.7	< – 26.8	< 21.0 [b]	
(103)	< – 21.5	< – 20.6	< 27.2 [b]	
(104)	< – 17.1	< – 17.6	< 30.2 [b]	
(105)	< – 13.2	< – 16.6	< 31.2 [b]	31.0 ± 0.7
(111)	< – 26.3	< – 26.2	< 21.6 [b]	
(112)	< – 19.2	< – 18.4	< 29.4 [b]	
(113)	< – 14.1	< – 14.0	< 33.8 [b]	
(114)	– 10.0 ± 0.1	– 12.0 ± 0.2	35.8 ± 0.3 [b]	35.6 ± 0.5
(121)	– 17.5 ± 0.2	– 17.1 ± 0.3	30.7 ± 0.4 [b]	30.5 ± 0.6
(122)	– 11.2 ± 0.1	– 10.8 ± 0.2	37.0 ± 0.4 [b]	36.8 ± 0.5
(123)	< – 8.9	< – 9.9	< 37.9 [b]	
(124)	< – 7.8	< – 11.6	< 36.2 [b]	
		≤ – 13.3 [c]	≤ 34.5 [b]	
(131)	– 9.7 ± 0.5	– 9.3 ± 0.5	38.5 ± 0.6 [b]	38.3 ± 0.7
(132)	< – 7.7	< – 8.0	< 39.8 [b]	
		< – 8.4 [c]	< 39.4 [b]	

(Continued on next page)

Table A-83: (continued)

Complex	$\log_{10} K_{s,1yz}$	$\log_{10} K^{\circ}_{s,1yz}$ (I = 0.5 M)	$\log_{10} \beta^{\circ}_{1yz}$	$\log_{10} \beta^{\circ}_{1yz}$ This review
Ternary hydroxide carbonate complexes				
(133)	< -6.8	< -9.2	< 38.6 [b]	
		< -10.9 [c]	< 36.9 [b]	
(141)	-7.2 ± 0.3	-7.2 ± 0.3	40.6 ± 0.5 [b]	40.4 ± 0.6
(142)	< -6.0	< -7.4	< 40.4 [b]	
		< -9.1 [c]	< 38.7 [b]	

a: Hydrolysis constants from [2000EKB/ALB], [2001NEC/KIM], [2002NEC/MUL].

b: The formation constants und upper limits given in [2005ALT/NEC] for $\log_{10} \beta^{\circ}_{1yz}$ are related to the solubility constant $\log_{10} K^{\circ}_{s,0} = -(47.8 \pm 0.3)$ that is based on hydrolysis constants which differ from those selected by this review. For reasons of consistency, the solubility constant is recalculated with the hydrolysis constants and SIT coefficients selected in the present review: $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$. This recalculated value is used to calculate the selected formation constants $\log_{10} \beta^{\circ}_{1yz}$ from the $\log_{10} K^{\circ}_{s,1yz}$ values in [2005ALT/NEC].

c: Calculated from solubility data in Na_2CO_3-NaOH solutions at $[CO_3^{2-}] = 1$ M.

Figure A-48: Solubility of ThO_2(am, hyd) under 0.1 bar CO_2(g) in 0.5 M NaCl [2005ALT/NEC]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$ recalculated in the present review from the authors' solubility data in carbonate-free solution.

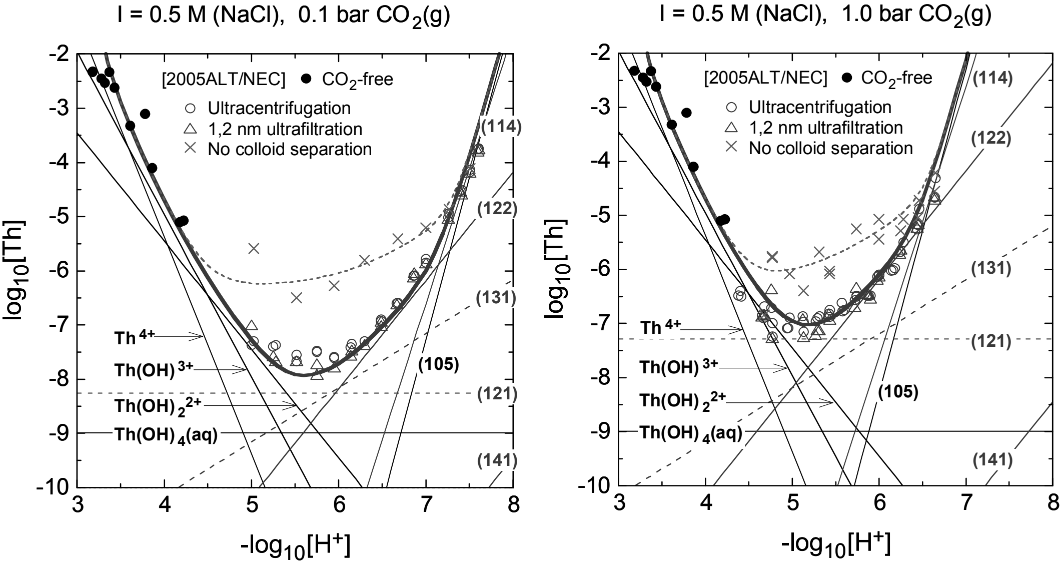


Figure A-49: Solubility of ThO_2(am, hyd) at I = 0.5 M ($NaHCO_3$-Na_2CO_3-NaOH-NaCl) and a total carbonate concentration of C_{tot} = 0.1, 0.04 and 0.015 M [2005ALT/NEC]. The corresponding data of [1994OST/BRU] at C_{tot} = 0.1 and I = 0.5 M ($NaClO_4$ media) and those determined in C_{tot} = 0.1 M ($NaHCO_3$-Na_2CO_3) without additional background electrolyte [1995RAI/FEL], [2005ALT/NEC] are shown for comparison.

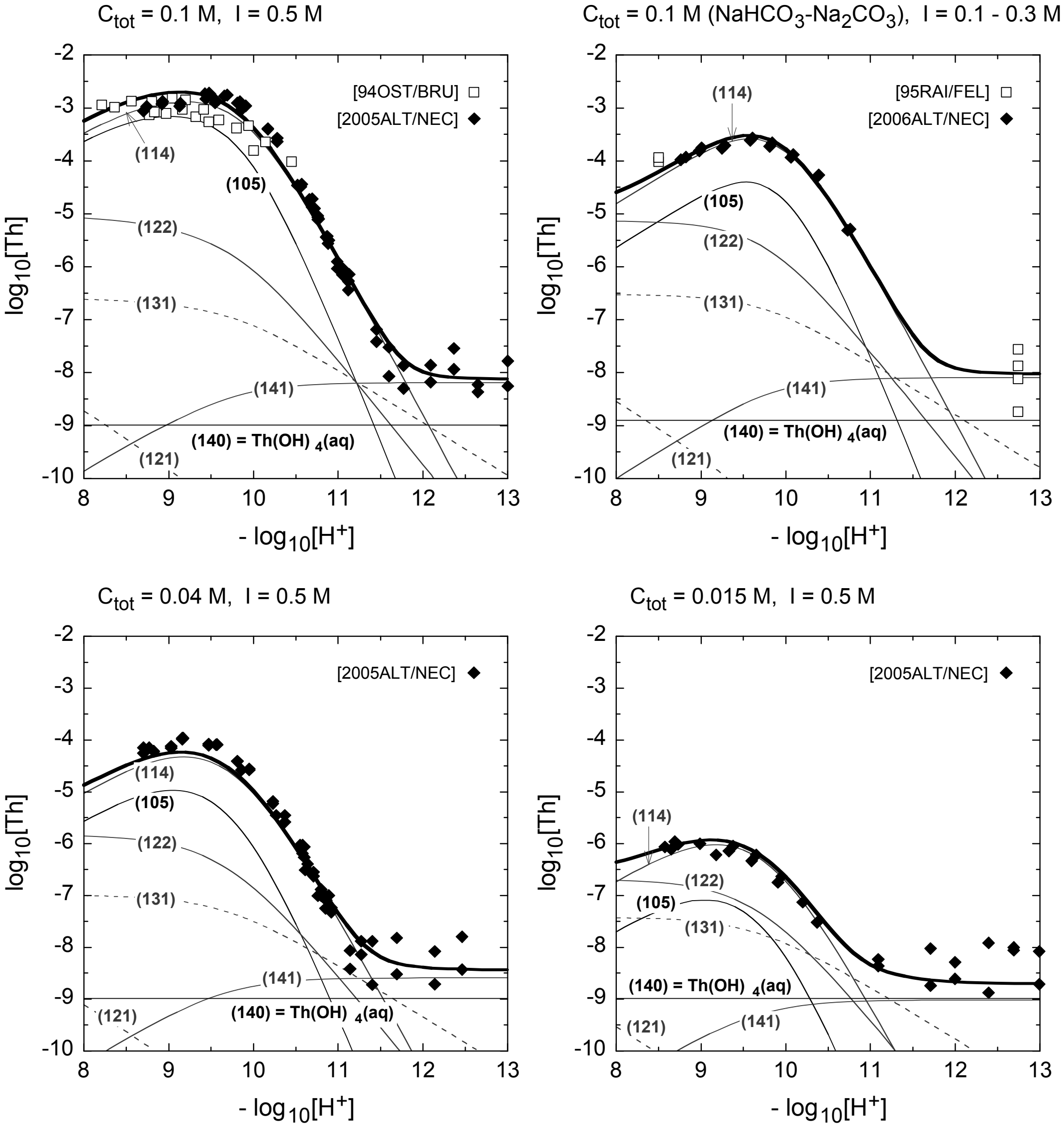


Figure A-50: Solubility of ThO$_2$(am, hyd) at a total carbonate concentration of C_{tot} = 0.02 M and constant ionic strengths of I = 0.1, 0.5, 2.0 and 4.0 M (NaHCO$_3$-Na$_2$CO$_3$-NaCl) [2006ALT/NEC]. The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{\circ}_{s,0}$ (aged ThO$_2$(am, hyd)) = – 47.5 selected in the present review.

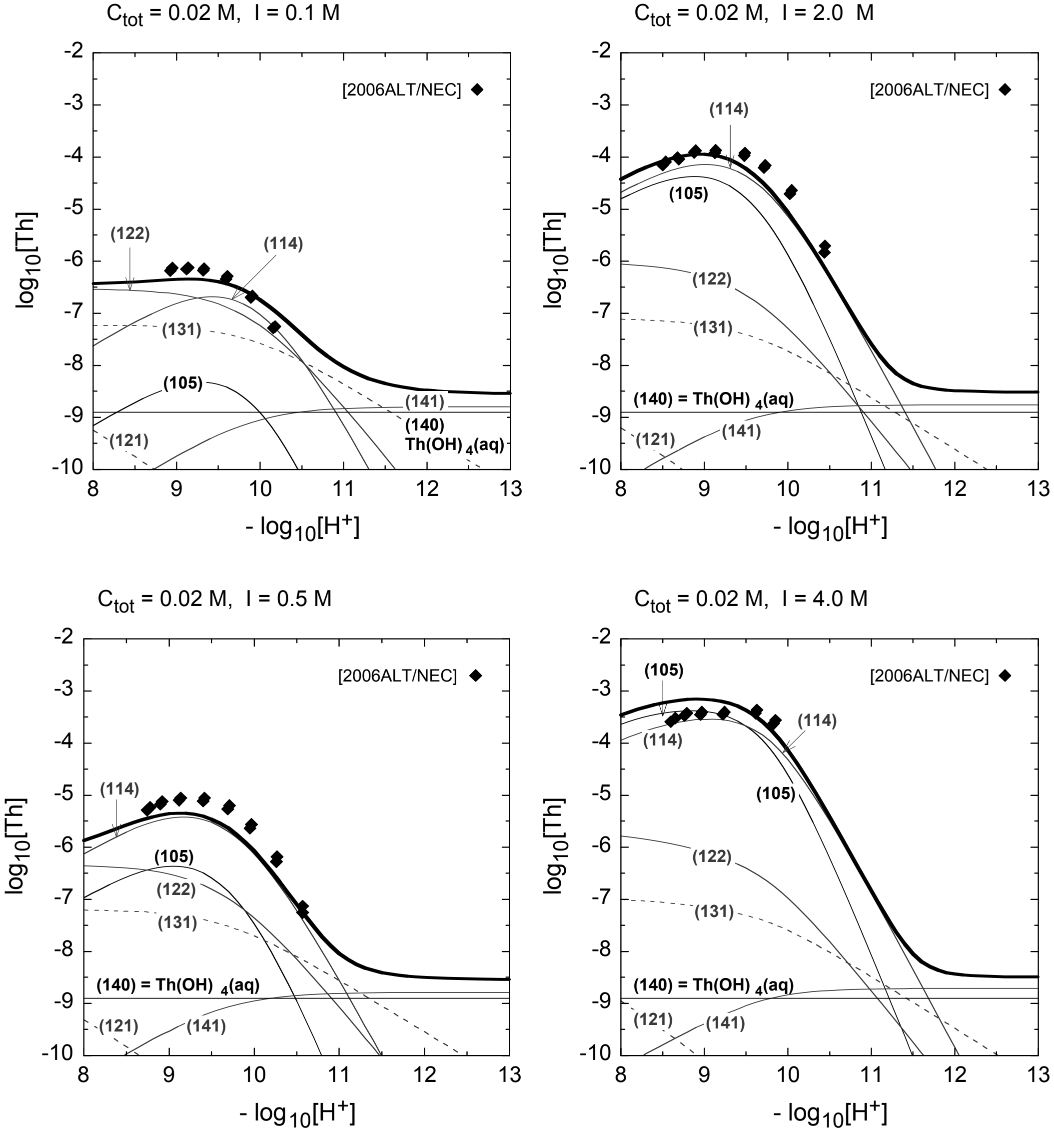
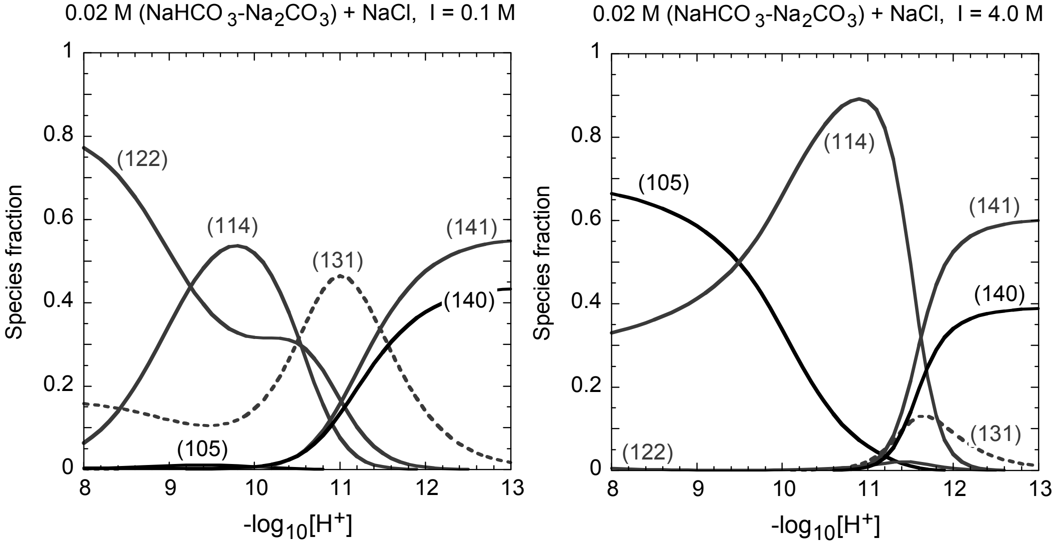


Figure A-50 shows the strong effect of ionic strength on the solubility. At constant carbonate and H^+ concentration of C_{tot} = 0.02 M and $-\log_{10}[H^+] = 9.5$, the solubility $\log_{10}[Th]$ increases from −6.2 to −3.4 when ionic strength is increased from I = 0.1 to 4.0 M. This effect is well predicted. It is due to the dramatic effect of ionic strength on the species distribution as illustrated in Figure A-51: Higher ionic strength favours the formation of the higher charged complexes $Th(CO_3)_5^{6-}$ and $Th(OH)(CO_3)_4^{5-}$ compared to $Th(OH)_2(CO_3)_2^{2-}$.

Figure A-51: Speciation at a total carbonate concentration of C_{tot} = 0.02 M and constant ionic strengths of I = 0.1 and 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl) [2006ALT/NEC]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and refer to solutions saturated with ThO_2(am, hyd).



[2005DAS/SIN]

The authors measured the pressure of CO_2(g) in the reaction Rb_2ThO_3(cr) according to the reaction:

$$ThO_2(cr) + Rb_2CO_3(cr) \rightleftharpoons Rb_2ThO_3(cr) + CO_2(g) \qquad (A.116)$$

The three solid phase compounds were mixed, pelleted, dried and heated in an alumina boat in a quartz tube attached to an all-metal vacuum system and the resultant CO_2(g) pressures measured manometrically at ten temperatures between 952 and 1098 K. Equilibration times were 200−400 h and attainment of equilibrium was checked by removal of some CO_2(g) and allowing the equilibrium to be attained again.

The Rb_2ThO_3 solid was prepared by heating rubidium nitrate and hydrated thorium nitrate with citric acid, which acts as an ignition agent, as described by [2000PUR/TYA] for $SrThO_3$(cr) and $BaThO_3$(cr). The X-ray diffraction pattern of the product were said to agree closely with those for the (hexagonal) cell reported by [1970HOP/SEE], but no details are given. The diffraction patterns of the mixture after equilibration showed no additional peaks from the initial mixture.

The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{CO_2}$/bar $= -13031/T + 8.915$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ ((A.116), T) = 249476 − 170.680 T (J·mol^{-1}). The Gibbs energy of the reaction $Rb_2O(l) + CO_2(g) \rightleftharpoons Rb_2CO_3(cr)$ over the experimental temperature range is given by −413796 + 173.100 T (J·mol^{-1}), where the data are taken from [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of Rb_2ThO_3(cr) from the component oxides is thus:

$$Rb_2O(l) + ThO_2(cr) \rightarrow Rb_2ThO_3(cr) \qquad (A.117)$$

$$[\Delta_r G_m]_{952K}^{1058K} ((A.117), T) = -164320 + 2.420\,T \text{ (J·mol}^{-1}\text{)}$$

Since the enthalpy of fusion of Rb_2O at 778 K is 20.0 kJ·mol^{-1}, [1982GLU/GUR], the Gibbs energy change for the metastable reaction involving Rb_2O(cr) would be approximately −144320 − 23.287 T (J·mol^{-1}) with an appreciable entropy change. Combination of the values for Reaction (A.117) with the values for $\Delta_f G_m^\circ$ (Rb_2O, l) from [1982GLU/GUR] and $\Delta_f G_m^\circ$ (ThO_2, cr) (this review) gives finally for the Gibbs energy of the formation reactions:

$$2Rb(l) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr) \qquad (A.118)$$

$$[\Delta_r G_m]_{952K}^{1058K} ((A.118), T) = -1688657 + 276.470\,T \text{ (J·mol}^{-1}\text{)}$$

and

$$2Rb(g) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr) \qquad (A.119)$$

$$[\Delta_r G_m]_{952K}^{1058K} ((A.119), T) = -1831523 + 424.248\,T \text{ (J·mol}^{-1}\text{)}$$

Both these equations are given since the pressure of Rb(g) over Rb(l) reaches 1 bar at *ca.* 967 K. The uncertainty in these values is estimated to be at least 11 kJ·mol^{-1}, mainly from the uncertainty in $\Delta_f H_m^\circ$ (Rb_2O, cr, 298.15 K) which is given as 8 kJ·mol^{-1} by [1982GLU/GUR]. These expressions correspond to a very negative value for the Gibbs energy of formation of Rb_2ThO_3, in comparison with the results reported in Section XII.1.2.2 for Cs_2ThO_3.

Since there are no other thermodynamic data for Rb_2ThO_3(cr), no further processing of these results is possible, and no values are selected for the review.

[2005HEN/TUT]

The study of the U(IV)-chloride system is relevant for the discussion of chloride complexes also for other tetravalent actinides, *viz.* Th^{4+}. The study describes the use of EXAFS methods to determine the composition and bond distances in the first coordination sphere of uranium. The complexes studied are weak and the authors have used factor analysis to separate the spectra for the two species present in the EXAFS test solutions. The number of coordinated water and chloride ligands was determined from these spectra. The authors report two alternative interpretations of their EXAFS results:

$[Cl^-]$ (M)	Number of H_2O ligands		Number of Cl^- ligands	
	Model 1	Model 2	Model 1	Model 2
3.0	8.5	8.5	0.3	0.3
6.0	7.6	6.7	0.8	1.4
9.0	6.1	5.2	2.1	2.7

The experimental U^{4+}–Cl^- distance indicates very clearly that chloride complexes are formed. The number of coordinated chloride ligands can be used to estimate the equilibrium constant; however, the coordination number is uncertain with an error of at least 20%. Using the data in 3 M chloride solution (HCl + LiCl), this review obtains:

$$K = \frac{0.3}{0.7 \times 3.0}\ \text{M}^{-1} = 0.14\ \text{M}^{-1}$$

This value is of the same order of magnitude as those obtained using equilibrium analytical methods. The conclusion of this review is that Hennig *et al.* have clearly demonstrated that U(IV) forms inner-sphere chloride complexes; this provides very strong indications that chloride complexes are formed also by Th^{4+}.

[2005MAZ/USH]

The standard enthalpies of formation of the two forms of $ThSiO_4$, thorite (tetragonal) and huttonite (monoclinic), and, independently, the enthalpy of transition between these two polymorphs, were obtained 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 $Li_2O{\cdot}2WO_3$ as solvent, at 1473 K for thorite and at 1673 K for huttonite. For these syntheses SiO_2 (α-quartz) with a reported purity greater than 99.9% and ThO_2(cr) with a reported purity greater than 99.99% (on the basis of the thorium content), thoroughly dried before use, were employed.

To obtain samples for analysis and calorimetry, crystals were ground (in an alumina mortar), washed with ethanol and dried at 1273 K. X-ray data showed that the tetragonal thorite samples were single phase, with lattice parameters $a = (7.129 \pm 0.001)$ Å and $c = (6.319 \pm 0.001)$ Å. As grown, huttonite crystals contained 8%

thorite, which could be entirely eliminated by a thermal treatment at 1773 K. The reported parameters of the pure monoclinic phase were: a = (6.774 ± 0.002) Å, b = (6.962 ± 0.002) Å, c = (6.495 ± 0.003) Å, β = (105.0 ± 0.1)°. For both species, reported lattice parameters were close to the literature values. Microprobe analyses indicated that the compounds were nearly stoichiometric, namely $Th_{1.005(3)}Si_{0.994(3)}O_4$ for thorite, and $Th_{1.011(5)}Si_{0.989(2)}O_4$, for huttonite.

Using commercial equipment, samples of both thorite and huttonite were heated from 298.15 K to (1774 ± 1) K. This temperature was chosen so that the conversion of thorite to huttonite was complete during the calorimetric run. In these experiments, the samples were of the same volume as that of the 5 mg α-alumina pellets used for the calibration of the equipment, and the completeness of the conversion of thorite to huttonite was checked by XRD.

The difference between the measured enthalpy contents gave the enthalpy of the transition of thorite to huttonite, with the assumption that the heat contents of the two isomorphs are the same. The experimental data (Table 2 of [2005MAZ/USH]) give a value of $\Delta_{trs}H_m$ ((A.120), 298.15 K) = (7.2 ± 7.4) $kJ\cdot mol^{-1}$ for the reaction:

$$ThSiO_4 \text{ (thorite)} \rightarrow ThSiO_4 \text{ (huttonite)} \qquad (A.120)$$

although the authors report a value of (7.4 ± 7.5) $kJ\cdot mol^{-1}$ in their text.

For the determination of the enthalpies of formation of the two polymorphs, a custom-built Tian-Calvet calorimeter was used, operating at 1080 K. The solvent, contained in a platinum crucible, was $2PbO\cdot B_2O_3$. This instrument was calibrated using the heat content of platinum between 298 and 1080 K. Attempts to measure solution enthalpies after equilibration of sample pellets above the solvent at the calorimeter temperature had to be abandoned as the melt vapours reacted with the samples. The reported results thus arise from experiments in which samples at room temperature (presumably 298.15 K) were dropped into the solvent at the calorimeter temperature.

For the reaction:

$$ThO_2(cr, 298.15\text{ K}) + SiO_2(\alpha, 298.15\text{ K}) \rightarrow ThSiO_4 \text{ (thorite or huttonite, 298.15 K)} \quad (A.121)$$

values of $\Delta_r H_m^\circ$ ((A.121), 298.15 K) = (19.6 ± 2.0) $kJ\cdot mol^{-1}$ for thorite and (26.3 ± 3.0) $kJ\cdot mol^{-1}$ for huttonite were obtained. This gives, for the transition, $\Delta_{trs}H_m^\circ$ ((A.120), 298.15 K) = (6.7 ± 3.6) $kJ\cdot mol^{-1}$, 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 $\Delta_f H_m^\circ$ (ThO_2, cr, 298.15 K) = −(1226.4 ± 3.5) $kJ\cdot mol^{-1}$ and $\Delta_f H_m^\circ$ (SiO_2, α, 298.15 K) = −(910.7 ± 1.0) $kJ\cdot mol^{-1}$ yields the values:

$$\Delta_f H_m^\circ (ThSiO_4\text{, thorite, 298.15 K}) = -(2117.5 \pm 4.2)\ kJ\cdot mol^{-1}$$

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

The authors also discuss the relationship between the standard enthalpies of the formation reactions of the various zircon-type orthosilicates $MSiO_4$ from the binary oxides and the ionic radii of the tetravalent M cations.

[2005RAI/YUI]

The paper discusses the solubility of Th-doped borosilicate glass containing 48.6% SiO_2 and 0.99% Th in a wide range of solutions with pH values from 0.5 to 12 and carbonate and bicarbonate concentrations up to 6.2 m and 1.0 m respectively. Equilibration times varied up to 93 days. The solubility was also approached from the over-saturation direction by spiking Th-doped glass suspensions with soluble thorium and following the changes in thorium concentrations with time. Membrane filters (0.0018 μm pore size) were used to separate solutions from suspensions in order to determine aqueous concentrations. A combination of X-ray diffraction and X-ray absorption spectroscopy (XAS) was used to characterise the solids and aqueous solutions. X-ray diffraction analyses did not detect any crystalline thorium solids indicating that the solids must be amorphous. No thermodynamic data are presented in the paper. Observed aqueous concentrations, a gradual decrease in aqueous thorium concentrations from the over-saturation direction, and XAS data strongly suggest that thorium in the solid and the aqueous phases around pH 1, is associated with silica. The data also indicate that thorium hydrous oxide is the possible solubility-controlling phase in the highly alkaline region.

[2006ALT/NEC]

In this study Altmaier *et al.* [2006ALT/NEC] extended their solubility measurements with $ThO_2{\cdot}xH_2O(am)$ in carbonate/bicarbonate buffers at I = 0.5 M [2005ALT/NEC] to a wider range of ionic strength, I = 0.1, 0.5, 2.0 and 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl) and I = 0.1 – 0.3 M (0.1 M $NaHCO_3$-Na_2CO_3 without additional background electrolyte). The authors derived an interaction coefficient of $\varepsilon(Na^+, Th(OH)(CO_3)_4^{5-})$ = – (0.22 ± 0.13) kg·mol^{-1} for the dominant (114) complex from their experimental data at I = 0.1 – 4.0 M ($\log_{10} K^\circ_{s,114}$ = – (11.9 ± 0.2), $\Delta\varepsilon$ = (0.22 ± 0.05) kg·mol^{-1}). This experimental SIT coefficient, close to the estimated value of $\varepsilon(Na^+, Th(OH)(CO_3)_4^{5-}) = -0.25$ kg·mol^{-1} used in [2005ALT/NEC], is selected in the present review. The close agreement between the experimental solubility data of [2006ALT/NEC] and the solubility calculated with the equilibrium constants and SIT coefficients selected in this review (including the pentacarbonate complex $Th(CO_3)_5^{6-}$ not taken into account by Altmaier *et al.*) are shown in the Appendix A entry for [2005ALT/NEC].

In addition, [2006ALT/NEC] contains a brief section on EXAFS measurements. The spectrum of a thorium solution in 1.0 M Na_2CO_3 / 0.1 M $NaHCO_3$ is consistent with those measured in [1997FEL/RAI] for thorium solutions at high carbonate or bicarbonate concentrations. The different EXAFS spectrum of a saturated solution taken from the solubility study at I = 0.5 M ($NaHCO_3$-Na_2CO_3-NaCl), C_{tot} = 0.1 M, and

– $\log_{10}[H^+] = 9.16$ shows that the pentacarbonate complex is not the dominant species in this sample which is consistent with the interpretation of the solubility data.

[2006NEC/ALT]

In this study ion interaction (SIT) coefficients for the Th^{4+} ion and trace activity coefficients in $NaClO_4$, $NaNO_3$ and NaCl solution were determined by solvent extraction with tri-*n*-butyl phosphate (TBP) at 22°C. The liquid-liquid phase equilibria between dilute to concentrated $NaClO_4$, $NaNO_3$ and NaCl solutions containing 0.01 – 0.02 M H^+ and $(1 - 8) \times 10^{-3}$ M Th^{4+} and organic phases consisting of 10 – 50 vol.% TBP in *n*-dodecane are given by:

$$Th^{4+}(aq) + 4\ X^-(aq) + n\ TBP(org) \rightleftharpoons ThX_4(TPB)_n(org) \qquad (A.122)$$

with $X^- = ClO_4^-$, NO_3^- and Cl^-. The thorium concentrations in the aqueous and organic phases were measured by ICP-MS. The organic phases were pre-equilibrated with corresponding aqueous HX-NaX solutions. To ensure that co-extraction of acids and sodium salts does not affect the free TBP concentration in the organic phase, the concentrations of HX and NaX in the organic phases were measured as well. Except of the experiments at higher perchlorate concentrations, which were not included in the data evaluation, this effect was found to be negligible. The conditional equilibrium constants $'K$ for a given aqueous ionic medium

$$'K = K\,[TBP(org)]^n = \frac{[ThX_4(TPB)_n(org)]}{[Th^{4+}]\,[X^-]^4} \qquad (A.123)$$

were extrapolated to zero ionic strength by linear SIT regression:

$$\log_{10}{'K} + 20D = \log_{10}{'K^\circ} + \varepsilon(Th^{4+}, X^-)\,m_{X^-} + 4\,\varepsilon(Na^+, X^-)\,m_{Na^+} \qquad (A.124)$$

The experimental data in 0.05 – 1.5 m $NaClO_4$ and in 0.05 – 3 m $NaNO_3$ yielded:

$$\varepsilon(Th^{4+}, NO_3^-) + 4\,\varepsilon(Na^+, NO_3^-) = (0.15 \pm 0.02)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(Th^{4+}, ClO_4^-) + 4\,\varepsilon(Na^+, ClO_4^-) = (0.74 \pm 0.04)\ kg{\cdot}mol^{-1}$$

and, with $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)\ kg{\cdot}mol^{-1}$ and $\varepsilon(Na^+, ClO_4^-) = (0.01 \pm 0.01)\ kg{\cdot}mol^{-1}$, the following interaction coefficients for the Th^{4+} ion:

$$\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg{\cdot}mol^{-1}$$

$$\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.06)\ kg{\cdot}mol^{-1}.$$

The interaction coefficient with perchlorate is in excellent agreement with $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg{\cdot}mol^{-1}$ estimated from the correlation between $\varepsilon(An^{4+}, ClO_4^-)$ and the ionic radii of the An^{4+} ions (*cf.* Section VI-3). The interaction coefficient $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg{\cdot}mol^{-1}$ [2006NEC/ALT] differs considerably from $\varepsilon(Th^{4+}, NO_3^-) = (0.11 \pm 0.02)\ kg{\cdot}mol^{-1}$ [1980CIA] adopted in the previous

NEA-TDB reviews. As the value of $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.31 \pm 0.12)$ kg·mol^{-1} follows the linear correlation between known values of $\varepsilon(\mathrm{M}^{Z+}, \mathrm{NO}_3^-)$ and $\varepsilon(\mathrm{M}^{Z+}, \mathrm{ClO}_4^-)$, it is considered to be more reliable than the value of $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.11 \pm 0.02)$ kg·mol^{-1} which strongly deviates from this correlation (*cf.* Section VI-3).

For aqueous phases containing NaCl, the distribution coefficients D_{Th} at $m_{\mathrm{NaCl}} < 3$ mol·kg^{-1} were too low to evaluate SIT coefficients in NaCl solution by linear regression, but the data determined by [2006NEC/ALT] in 2.5 − 5.0 m NaCl were found to be compatible with the SIT coefficients selected in the NEA-TDB reviews, $\varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-) + 4\,\varepsilon(\mathrm{Na}^+, \mathrm{Cl}^-) = (0.37 \pm 0.04)$ kg·mol^{-1}.

The method used in [2006NEC/ALT] was also tested for the extraction of $\mathrm{HClO_4}$ and $\mathrm{HNO_3}$ from aqueous $\mathrm{NaClO_4}$ and $\mathrm{NaNO_3}$ solutions and U(VI) in dilute to concentrated $\mathrm{NaClO_4}$, $\mathrm{NaNO_3}$ and chloride solutions (NaCl, $\mathrm{MgCl_2}$, $\mathrm{CaCl_2}$). The variation of the distribution coefficients was in excellent agreement with calculations based on SIT coefficients from the NEA-TDB reviews: $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, $\varepsilon(\mathrm{H}^+, \mathrm{NO}_3^-) = (0.07 \pm 0.01)$ kg·mol^{-1}, $\varepsilon(\mathrm{UO}_2^{2+}, \mathrm{ClO}_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(\mathrm{UO}_2^{2+}, \mathrm{NO}_3^-) = (0.24 \pm 0.03)$ kg·mol^{-1}, and $\varepsilon(\mathrm{UO}_2^{2+}, \mathrm{Cl}^-) = (0.21 \pm 0.02)$ kg·mol^{-1} [1992GRE/FUG], [2003GUI/FAN].

It is to be noted that the ion interaction coefficients for Th^{4+} and UO_2^{2+} discussed above refer to a strict ion interaction approach which does not account for the formation of chloride and nitrate complexes. This review has re-evaluated the Th(IV) extraction data from aqueous nitrate phases using also the complexation model. Figure A-52 shows that the experimental data of [2006NEC/ALT] in 0.05 − 3 M $\mathrm{NaNO_3}$ + 0.02 M $\mathrm{HNO_3}$ can be described equally well with both approaches.

Using the complexation model (Figure A-52-b), the interaction coefficient of Th^{4+} in nitrate solution is set equal to the interaction coefficient in non-complexing perchlorate solution:

$$\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$$

and the interaction of Th^{4+} with nitrate is ascribed to the reactions:

$$\mathrm{Th}^{4+} + n\,\mathrm{NO}_3^- \rightleftharpoons \mathrm{Th(NO_3)}_n^{4-n} \qquad \text{(A.125)}$$

with $\Delta\varepsilon_{n=1} = -(0.21 \pm 0.05)$ kg·mol^{-1} and $\Delta\varepsilon_{n=2} = -(0.41 \pm 0.13)$ kg·mol^{-1} in $\mathrm{HNO_3}$ media and $\Delta\varepsilon_{n=1} = -(0.10 \pm 0.10)$ kg·mol^{-1} and $\Delta\varepsilon_{n=2} = -(0.19 \pm 0.16)$ kg·mol^{-1} in $\mathrm{NaNO_3}$ media adopted from the analogous reactions of U(IV) [1992GRE/FUG]. Up to nitrate concentrations of 1.0 M, the distribution coefficients D_{Th} are well described with the equilibrium constant $\log_{10} \beta_1^{\circ}$ ((A.125), $n = 1$) = (1.5 ± 0.2) (dotted line in Figure A-52-b). The fit including experimental data at higher nitrate concentrations (dashed line in Figure A-52-b) gives also the formation constants of the complexes $\mathrm{Th(NO_3)}_2^{2+}$ and $\mathrm{Th(NO_3)}_3^{+}$:

$\log_{10} \beta_1^\circ$ (A.125) = (1.3 ± 0.2),

$\log_{10} \beta_2^\circ$ (A.125) = (2.3 ± 0.4), and

$\log_{10} \beta_3^\circ$ (A.125) = (3.0 ± 0.5).

An estimate of $\varepsilon(\mathrm{Th(NO_3)_3^+}, \mathrm{NO_3^-}) = \varepsilon(\mathrm{Th(NO_3)_3^+}, \mathrm{ClO_4^-}) = (0.25 \pm 0.15)$ kg·mol^{-1}, *i.e.*, $\Delta\varepsilon_{n=3} = -(0.33 \pm 0.20)$ kg·mol^{-1} in $\mathrm{NaNO_3}$ solution, is used for ionic strength corrections of the third complex which becomes significant at $[\mathrm{NO_3^-}] > 2$ M. The equilibrium constants for the first and second complex are close to the values selected in the NEA-TDB review of uranium for the analogous U(IV) nitrate complexes which have been studied by different authors and different experimental methods at widely varying ionic strength ($\log_{10} \beta_1^\circ(\mathrm{U(NO_3)^{3+}}) = (1.47 \pm 0.13)$, $\log_{10} \beta_2^\circ(\mathrm{U(NO_3)_2^{2+}}) = (2.30 \pm 0.35)$ [1992GRE/FUG]).

A considerably different value of $\log_{10} \beta_1^\circ(\mathrm{Th(NO_3)^{3+}}) = 2.0$ was obtained from the TTA extraction study of [1950DAY/STO] who calculated $\beta_1 = 4.73$ M^{-1} from the variation of the distribution coefficient in 0.5 M $\mathrm{HClO_4}$-$\mathrm{HNO_3}$. The alternative evaluation of their experimental data with the ion interaction approach yields a strongly negative value of $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-}) = -0.61$ kg·mol^{-1}(*cf.* Appendix review of [1950DAY/STO]). Figure A-53 shows that both the calculations with the data obtained from the study of [1950DAY/STO], either using $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-}) = -0.61$ kg·mol^{-1} (ion interaction model) or using $\log_{10} \beta_2^\circ = 2.0$ and $\Delta\varepsilon_{n=1} = -(0.21 \pm 0.05)$ kg·mol^{-1} [1992GRE/FUG] (nitrate complexation model) significantly overpredict the effect of nitrate interaction or complexation on the distribution coefficients determined by [2006NEC/ALT] for aqueous phase containing 0.05–3 M $\mathrm{NaNO_3}$ + 0.02 M $\mathrm{HNO_3}$. In particular the negative value of $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-}) = -0.61$ kg·mol^{-1} is extremely inappropriate to model the results at nitrate concentrations above 0.5 M.

Figure A-52: Distribution coefficients of Th(IV) in the TBP extraction study of [2006NEC/ALT] (aqueous phase: 0.05−3 M $NaNO_3$ + 0.02 M HNO_3; organic phase: TBP/*n*-dodecane). Experimental data and recalculation a) with the ion interaction model, b) with the nitrate complexation model. (All calculations are performed on the molal scale and back-transformed to the molar scale for direct comparison with the experimental data.)

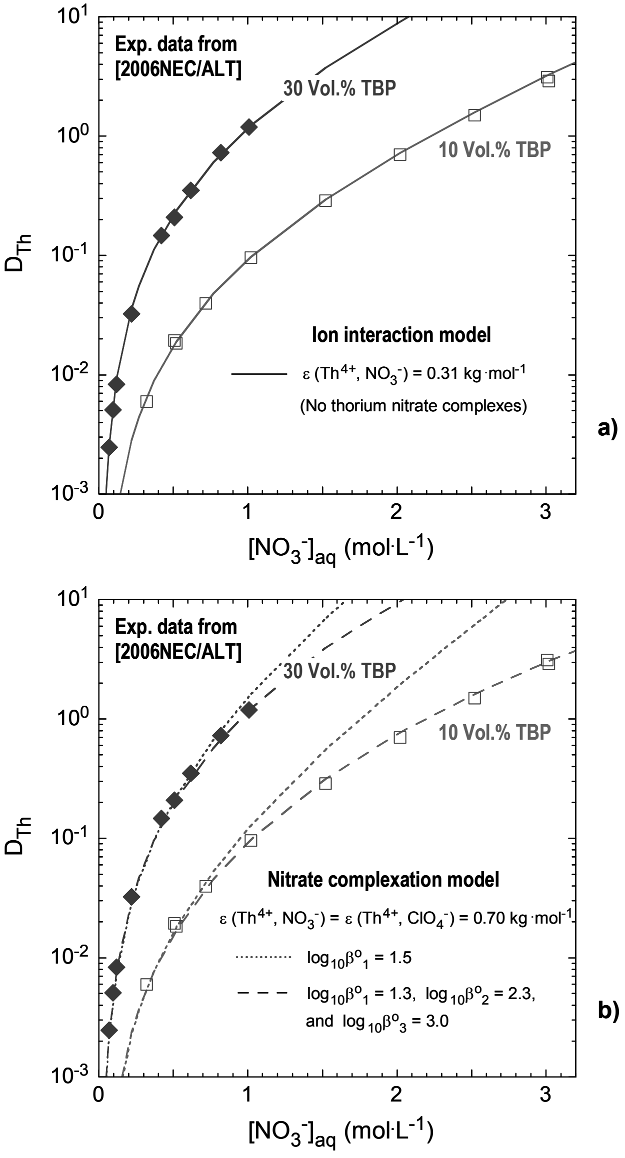
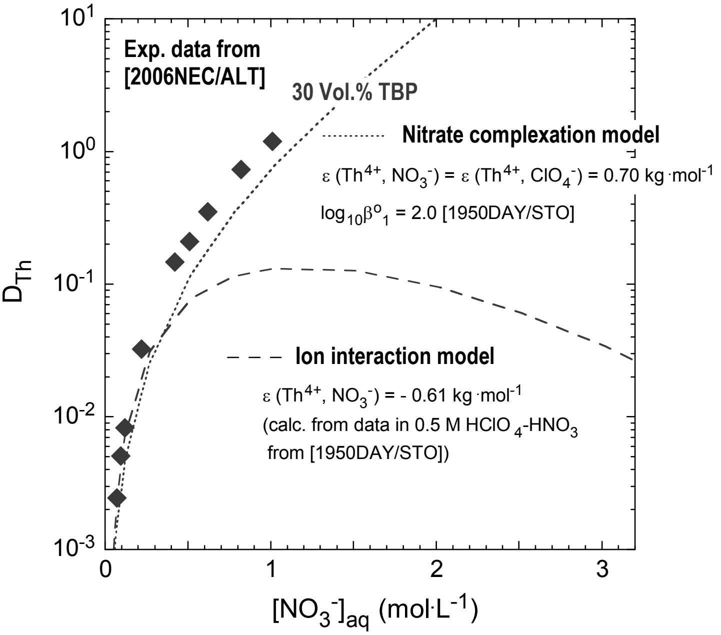


Figure A-53: Comparison of experimental distribution coefficients of Th(IV) in the TBP extraction study of [2006NEC/ALT] (aqueous phase: 0.05 – 3 M $NaNO_3$ + 0.02 M HNO_3; organic phase: TBP/*n*-dodecane) and calculations with the data obtained from the TTA extraction study of [1950DAY/STO], either $\varepsilon(Th^{4+}, NO_3^-) = -0.61$ (ion interaction model) or $\log_{10} \beta_1^\circ = 2.0$ (nitrate complexation model).



[2007BRE/ALT]

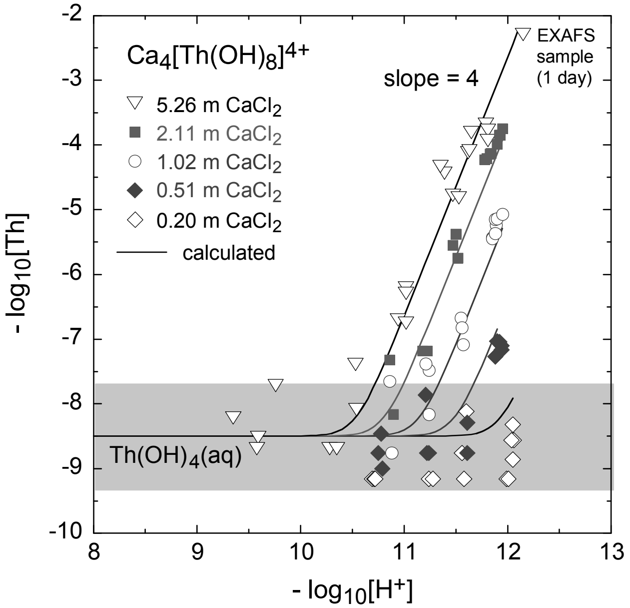
Brendebach *et al.* [2007BRE/ALT] report unexpectedly high solubilities of Zr(IV) and Th(IV) hydrous oxides in alkaline $CaCl_2$ solutions kept under an argon atmosphere at (22 ± 2)°C (for Zr(IV) at $-\log_{10}[H^+] = 10$ to 12 in 0.2, 0.5 and 2.0 M $CaCl_2$ and for Th(IV) at $-\log_{10}[H^+] = 11$ to 12 in 0.5 to 4.5 M $CaCl_2$). The dominant aqueous species are identified as ternary Ca-M(IV)-OH complexes, $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$, respectively. The EXAFS spectra of four Zr(IV) solutions and a 4.3×10^{-3} M Th(IV) solution at $-\log_{10}[H^+] = 12.2$ in 4.5 M $CaCl_2$ (the latter is oversaturated with regard to the solubility of calcium hydroxychlorides at this pH) show two coordination shells. The numbers of oxygen atoms in the first coordination sphere detected by EXAFS, $N_O = (6.6 \pm 1.2)$ for Zr and $N_O = (8.6 \pm 1.2)$ for Th, are consistent with 6 and 8 OH^- ligands as derived from the respective slopes of 2 and 4 in the solubility curves of $\log_{10}[M]_{tot}$ versus $-\log_{10}[H^+]$. The EXAFS spectra also show a second co-ordination shell of Ca^{2+} ions, with $N_{Ca} = 3$ (2.7 ± 0.6) at a distance of $R_{Zr\text{-}Ca} = (3.38 \pm 0.02)$ Å for the zirconium complex and $N_{Ca} = 4$ (3.8 ± 0.5) at a distance of $R_{Th\text{-}Ca} = (3.98 \pm 0.02)$ Å for the thorium complex. The presence of dominating amounts of polynuclear hydrolysis species and the formation of complexes with chloride ligands can be excluded. The ternary $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$ complexes, where the central $[Zr(OH)_6^{2-}]$ and $[Th(OH)_8^{4-}]$ complexes are stabilised by associated Ca^{2+} ions, probably have distorted rutile- and fluorite-type structures with the Ca^{2+} ions bound to coordination polyhedra edges.

The authors have used the SIT to describe the measured solubilities. The thorium data (Figure A-54) are well described with an equilibrium constant of $\log_{10} K^{\circ}_{s,(4,1,8)} = (1.8 \pm 0.5)$ for the reaction

$$Th(OH)_4(am) + 4Ca^{2+} + 4OH^- \rightleftharpoons Ca_4[Th(OH)_8]^{4+}$$

and $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-) = -(0.01 \pm 0.10)$ kg·mol^{-1}. However, the ion interaction coefficient depends strongly on the data in 4.5 M $CaCl_2$, *i.e.* at $I_m = 15.8$ mol·kg^{-1} which is far above the validity range of the SIT. The data reported in [2007BRE/ALT] may be used as guidance in estimating the solubility of thorium in salt solutions containing cementitious waste forms.

Figure A-54: Experimental solubility data reported in [2007BRE/ALT] for Th(IV) hydrous oxide in 0.2 to 4.5 M $CaCl_2$ solutions (after equilibration times of 14 to 198 days, except of the EXAFS sample which was measured after only one day); the calculated curves are based on the proposed SIT model parameters.



[2007HEN/SCH]

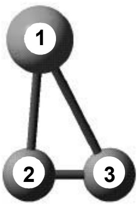
Hennig *et al.* have investigated test solutions of 0.05 M Th(IV) at pH close to 1 and with total concentrations of sulphate in the range $0.90 \le [SO_4^{2-}] + [HSO_4^-] \le 2.0$ M, using EXAFS methodology to obtain information on the stoichiometry, geometry and mode of coordination in the Th(IV) sulphato complexes formed under these experimental conditions; only the EXAFS results of Th(IV) sulphato complexes will be discussed.

There are two S−Th distances at 3.81 and 3.14 Å, respectively, consistent with a complex that contains both unidentate and bidentate sulphate coordination. The numbers of unidentate Th−S distances reported in the two test solutions are 3.7 and 3.8, respectively; the numbers of bidentate Th−S distances in the same solutions are 0.9 and 1.6, respectively. These numbers indicate the presence of complexes with the stoichiometry $Th(SO_4\text{-uni})_4(SO_4\text{-bi})(OH_2)_x$ and $Th(SO_4\text{-uni})_4(SO_4\text{-bi})_2(OH_2)_y$. The number of coordinated oxygen atoms is close to 9, indicating that there are some coordinated water ligands present in the sulphato complexes. However, the uncertainty in the number of Th−S and Th−O distances is fairly large (± 15%), making a more quantitative estimate of the constitution of the complexes difficult. It is of interest to note that the proposed mode of sulphate coordination is similar to that found in the structure of $Cs_2[Th(SO_4)_3]\cdot(H_2O)_3$, *cf.* Figure IX-1) where there are three bidentate and two unidentate sulphato ligands and two water coordinated to Th. The composition of the test solutions and the measured pH in the test solutions are consistent with the formation of strong sulphato complexes, but it is not possible to use these data to estimate equilibrium constants.

[2008KOV/KON]

The geometry and vibrations of the ThC_2 and ThC_4 gaseous molecules have been derived from quantum chemical calculations, using second-order perturbation theory. The results indicate an asymmetric essentially L-shaped structure for $ThC_2(g)$ and a symmetric planar fan-type structure (with C_{2v} symmetry) for $ThC_4(g)$.

The details of the structures are given in Table A-84, where the numbering of the carbon atoms is as follows in the schematic models:



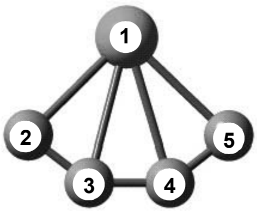
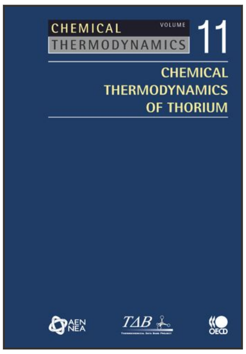


Table A-84: Molecular parameters of $ThC_2(g)$ and $ThC_4(g)$.

Parameter	$ThC_2(g)$	$ThC_4(g)$
	Symmetry C_s	Symmetry C_{2v}
r (Th-C2) (Å)	2.155	2.365
r (Th-C3) (Å)	2.473	2.532
Angle Th-C2-C3	88.1°	82.1°
Angle C2-Th-C3	31.3°	30.2°
Angle C2-Th-C5		91.6°
Angle C3-Th-C4		31.2°
Harmonic vibration frequencies (degeneracies) (cm^{-1})	632(1) 210(1) 1649(1)	1818(1) 1706(1) 1054(1) 642(1) 475(1) 393(1) 372(1) 499(1) 280(1)

[1995ROS/BAL] and [1996ROS/BAL] have found from similar *ab initio* calculations that $YC_2(g)$ and $LaC_2(g)$ have symmetrical C_{2v} fan-shaped structures. Kovács and Konings indicate that for $ThC_2(g)$, this structure is stable, but lies *ca.* 7.7 kJ·mol^{-1} (644 cm^{-1}) above the asymmetric configuration described above.

The effective charge on the thorium atom is found to be 1.66 for $ThC_2(g)$ and 1.60 for $ThC_4(g)$. For this reason, [2008KOV/KON] used the electronic levels of ThO(g), where the thorium atom is divalent, in calculating the thermal functions of the carbide molecules, and we have followed the same procedure, as discussed in sections XI.1.2.1 and XI.1.2.2. However, as noted there, the calculated entropies of the reactions $Th(g) + nC(cr) \rightleftharpoons ThC_n(g)$, $n = 2, 4$ are noticeably different (by *ca.* 30 and −17 $J \cdot K^{-1} \cdot mol^{-1}$ respectively) from those derived from the vaporisation experiments of [1964JAC/BAR] and [1974KOH/STE].



Chemical Thermodynamics of Thorium, Volume 11

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