

## X Thorium Group 15 compounds and complexes

### X.1 Nitrogen compounds and complexes

#### X.1.1 Solid and gaseous thorium nitrides

There are two solid nitrides, the semimetal compound ThN(cr), and the Th(IV) compound Th<sub>3</sub>N<sub>4</sub>(cr), both of which have a small range of homogeneity at high temperatures. Benz and Zachariassen [1966BEN/ZAC] showed that the phase previously thought to be Th<sub>2</sub>N<sub>3</sub>(cr) is in fact the oxynitride Th<sub>2</sub>N<sub>2</sub>O(cr) (see Section X.1.1.4).

##### X.1.1.1 Thorium mononitride ThN(cr)

Thorium mononitride has a face centred cubic NaCl structure,  $Fm\bar{3}m$ , with  $a = (5.159 \pm 0.001) \text{ \AA}$  [1966ARO/AUS], [1972DAN/NOV] and is isostructural with all the lower actinide mononitrides [1967BEN/HOF], [1967AUS/ARO].

The low-temperature heat capacity of ThN(cr) was measured by Danan *et al.* [1972DAN/NOV] between 7 and 300 K and by de Novion and Costa between 3 and 9 K [1970NOV/COS]. The results of [1972DAN/NOV] lead to  $S_m^\circ(\text{ThN, cr, 298.15 K}) = (56.0 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Dell [1973DEL] cites a further value of  $S_m^\circ(\text{ThN, cr, 298.15 K}) = (57.3 \pm 0.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  from unpublished heat capacity measurements of Dell and Martin, in marginal agreement with the value of [1972DAN/NOV]. The latter is selected here with larger uncertainty limits, thus:

$$S_m^\circ(\text{ThN, cr, 298.15 K}) = (56.0 \pm 1.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The heat capacity values given by the two authors agree excellently and provide the selected value:

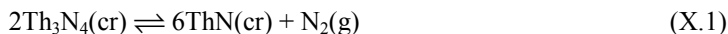
$$C_{p,m}^\circ(\text{ThN, cr, 298.15 K}) = (45.0 \pm 1.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Ono *et al.* [1973ONO/KAN] have measured the heat capacity of ThN(cr) from *ca.* 450 to 850 K. They fitted their results to an equation which gives a rather lower  $C_{p,m}^\circ$  at 298.15 K than the selected value, so their data have been refitted with a constraint of  $C_{p,m}^\circ(\text{ThN, cr, 298.15 K}) = 45.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , see Appendix A, to give the following equation, which is extrapolated to 2000 K:

$$[C_{p,m}^\circ]_{298.15\text{K}}^{2000\text{K}}(\text{ThN, cr, } T) = 47.836 + 1.3775 \times 10^{-2} T - 6.172 \times 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Adachi *et al.* [2005ADA/KUR] have made a molecular dynamics calculation for thorium mononitride in the temperature range from 300 to 2800 K to evaluate the thermophysical properties including heat capacity ( $C_{v,m}^\circ$ ). An electronic contribution, based on the very low temperature results of de Novion and Costa [1970NOV/COS] was added to calculate  $C_{p,m}^\circ$ . However, as noted in Appendix A, these calculated  $C_{p,m}^\circ$  values are *ca.*  $10 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  smaller than the experimental values of [1973ONO/KAN] discussed above, and have been discounted.

There have been no calorimetric studies of the enthalpy of formation of ThN(cr) and the enthalpy of formation is derived from the nitrogen pressures of the decomposition of Th<sub>3</sub>N<sub>4</sub>(cr). These have been measured by Aronson and Auskern [1966ARO/AUS] (1723 to 2073 K) and by Kusakabe and Imoto [1971KUS/IMO], [1972KUS/IMO] (1723 to 2170 K) with reasonable agreement. The compositions of the solid-phase compositions were not established in either of these studies but, from the investigation of the Th-N system by Benz *et al.* [1967BEN/HOF], it seems clear that there will be significant non-stoichiometry in both ThN(cr) and Th<sub>3</sub>N<sub>4</sub>(cr) above *ca.* 1723 K. Thus only the lowest temperature points of the two studies [1966ARO/AUS] and [1971KUS/IMO] have been utilised. For the reaction:



the mean value of  $\Delta_r G_m^\circ$  ((X.1), 1723 K) of  $(65.5 \pm 5.4) \text{ kJ}\cdot\text{mol}^{-1}$  has been combined with the thermal data to give:

$$\Delta_r H_m^\circ((\text{X.1}), 298.15 \text{ K}) = (326.2 \pm 52.0) \text{ kJ}\cdot\text{mol}^{-1}$$

and thus

$$\Delta_f H_m^\circ(\text{ThN, cr}, 298.15 \text{ K}) = -(381.2 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1},$$

which is the selected value, where the uncertainties include those attributable to possible errors in the heat capacity data.

Sedmidubský *et al.* [2005SED/KON] have made *ab initio* calculations of the enthalpies of formation of the actinide mononitrides, using density functional theory. They find good agreement with the experimental data for UN(cr) and NpN(cr), but larger differences for both ThN(cr) and PuN(cr). For ThN(cr) they calculate  $\Delta_f H_m^\circ(\text{ThN, cr}, 298.15 \text{ K}) = -347.9 \text{ kJ}\cdot\text{mol}^{-1}$ . The uncertainty was not given by the authors, but is estimated by the review to be at least  $15.0 \text{ kJ}\cdot\text{mol}^{-1}$ . Their value of  $\Delta_f H_m^\circ(\text{ThN, cr}, 298.15 \text{ K})$  is indeed, notably more positive than that derived above. However, if the enthalpy of formation of ThN(cr) were as large as  $-347.9 \text{ kJ}\cdot\text{mol}^{-1}$ , the decomposition pressure of N<sub>2</sub>(g) in Reaction (X.1) at 1723 K would be as low as  $10^{-8}$  bar, compared to the experimental values of *ca.*  $10^{-2}$  bar from the consistent data of [1966ARO/AUS] and [1971KUS/IMO], assuming the two consistent measurements of the enthalpy of formation of Th<sub>3</sub>N<sub>4</sub>(cr) (see Section X.1.1.3) are correct. The selected value is therefore the value derived above,  $\Delta_f H_m^\circ(\text{ThN, cr}, 298.15 \text{ K}) = -(381.2 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$ .

Olson and Mulford [1965OLS/MUL] and Benz *et al.* [1967BEN/HOF] have measured nitrogen pressures from the decomposition of ThN(cr) at very high temperatures (2689 to 3096 K), with good agreement. However under these conditions ThN(cr) is, according to the phase diagram given by [1967BEN/HOF], substantially hypostoichiometric and Th(l) dissolves appreciable amounts of nitrogen, so no reliable information on stoichiometric ThN(cr) can be derived from these measurements.

It may be noted that Rand [1975RAN] combined all these investigations [1966ARO/AUS], [1965OLS/MUL], [1967BEN/HOF], [1971KUS/IMO] of the nitrogen decomposition pressures of ThN(cr) and Th<sub>3</sub>N<sub>4</sub>(cr) with the extensive phase diagram data reported by Benz *et al.* [1967BEN/HOF], [1972BEN], and gives an approximate Gibbs-energy diagram, showing the values of the nitrogen potential  $\Delta G_{N_2}$  as a function of temperature for the Th + ThN<sub>1-x</sub>, ThN<sub>1±x</sub> single-phase and ThN<sub>1+x</sub>-Th<sub>3</sub>N<sub>4</sub> regions. Such details of the non-stoichiometric regions are not of immediate concern to this review and are mentioned for information only.

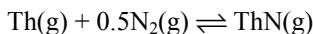
Benz *et al.* [1967BEN/HOF] have studied the evaporation of ThN<sub>1±x</sub>(cr), which occurs mainly by decomposition to Th(g) and N<sub>2</sub>(g), with a small amount of ThN(g) see Section X.1.1.2). They observed that at 2200 K the congruently evaporating composition is ThN<sub>0.88</sub>, which as shown by Rand [1975RAN], is consistent with the phase diagram observations of Benz *et al.* [1967BEN/HOF].

The data of [1965OLS/MUL] and [1967BEN/HOF] show that ThN melts effectively congruently under 1–2 bar pressure of nitrogen at (3080 ± 30) K. The above selections yield:

$$\Delta_f G_m^\circ(\text{ThN, cr, 298.15 K}) = -(353.6 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### X.1.1.2 Gaseous thorium mononitride ThN(g)

In a mass-spectrometric study, Gingerich [1968GIN] has detected very small amounts of ThN(g) in the vapour over a mixture ThP(cr) + BN(cr) and gives values for the partial pressures of the species in the gaseous equilibrium:



at 2702 and 2745 K, using a silver calibration to convert from ion intensities to partial pressures. Both Gingerich [1968GIN] and Rand [1975RAN] have estimated molecular parameters for ThN(g) by a comparison of the values for MN(g) and MO(g) species of other tetravalent metals. As Gingerich does not quote his values, our calculations are based on the parameters given by Rand [1975RAN]. However those values of  $r = 1.93 \text{ \AA}$  and  $B = 0.3 \text{ cm}^{-1}$  are not consistent, so we have changed  $B$  to the value consistent with  $r = 1.93 \text{ \AA}$ , *viz.*  $B = 0.3426 \text{ cm}^{-1}$ . The remaining parameters are  $\omega = 775 \text{ cm}^{-1}$ ,  $\omega x = 3 \text{ cm}^{-1}$ , ground-state degeneracy = 2. Our value of the Gibbs energy function at 2700 K is *ca.*  $5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  greater than that quoted by [1975RAN]. The thermal functions from the selected parameters give  $S_m^\circ(\text{ThN, g, 298.15 K}) = (245.8 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and lead finally to  $\Delta_f H_m^\circ(\text{ThN, g, 298.15 K}) = (502 \pm 25) \text{ kJ}\cdot\text{mol}^{-1}$  by a third-law calculation.

This value indicates that the gaseous nitride is always a very minor species (1 to 100 ppm) compared with Th(g) and N<sub>2</sub>(g) at the very high temperatures where vapourisation of ThN is at all appreciable. In view of this and the numerous uncertainties in

both the experimentation (paucity of data, ionisation cross-sections *etc.*) and the thermal functions for ThN(g), the above values are given for information only.

### X.1.1.3 Th<sub>3</sub>N<sub>4</sub>(cr)

Th<sub>3</sub>N<sub>4</sub>(cr) has a rhombohedral structure, space group  $R\bar{3}m$ ; the lattice parameters for the corresponding hexagonal cell are  $a = (3.875 \pm 0.002) \text{ \AA}$  and  $c = (27.39 \pm 0.04) \text{ \AA}$  [1971BOW/ARN]. Juza and Gerke [1968JUZ/GER] have reported, in addition, the preparation of a  $\beta$ -modification of Th<sub>3</sub>N<sub>4</sub>(cr), with a monoclinic distortion of the La<sub>2</sub>O<sub>3</sub> lattice with  $a = 6.952$ ,  $b = 3.830$ ,  $c = 6.206 \text{ \AA}$ ,  $\beta = 90.71^\circ$ . It transforms monotropically to  $\alpha$ -Th<sub>3</sub>N<sub>4</sub>(cr).

The selected heat capacities and entropy at 298.15 K are those from the unpublished measurements of Dell and Martin cited by Dell [1973DEL] but with substantially increased uncertainties in view of the total lack of details of this study [1973DEL].

$$C_{p,m}^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = (147.7 \pm 8.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = (183.1 \pm 15.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Ono *et al.* [1973ONO/KAN] have measured the heat capacity of Th<sub>3</sub>N<sub>4</sub>(cr) from *ca.* 450 to 850 K. They fitted their results to an equation which gives a rather lower  $C_{p,m}^\circ$  at 298.15 K than the selected value, so their data have been refitted with a constraint of  $C_{p,m}^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = 147.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , see Appendix A, to give the following equation, which is extrapolated to 2000 K:

$$[C_{p,m}^\circ]_{298.15\text{K}}^{2000\text{K}}(\text{Th}_3\text{N}_4, \text{cr}, T) = 181.517 + 26.181 \times 10^{-3} T - 37.000 \times 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Sato [1939SAT] has measured the mean heat capacity of a sample whose composition was essentially equivalent to a mixture of Th<sub>3</sub>N<sub>4</sub>(cr) and ThO<sub>2</sub>(cr) over three temperature ranges from 273.2 to 776.2 K. However as noted in Appendix A, it is not clear whether this was simply a mixture or a solid solution of these phases (and thus close to the composition of the oxynitride Th<sub>2</sub>N<sub>2</sub>O(cr)), and these data have not been considered further in the review.

Neumann *et al.* [1932NEU/KRO], [1934NEU/KRO] have reported two separate measurements of the enthalpy of formation of Th<sub>3</sub>N<sub>4</sub>(cr) – see Appendix A. The first, by combustion of thorium in nitrogen, gives  $\Delta_f H_m^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = -(1306.3 \pm 16.3) \text{ kJ}\cdot\text{mol}^{-1}$  (average of three experiments), while the second, by combustion of Th<sub>3</sub>N<sub>4</sub>(cr) in oxygen (one experiment only) gives  $\Delta_f H_m^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = -(1308.1 \pm 11.5) \text{ kJ}\cdot\text{mol}^{-1}$ . The selected value results from giving equal weight to each of the four individual measurements:

$$\Delta_f H_m^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = -(1306.8 \pm 15.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

The measurements of the nitrogen dissociation pressure of Th<sub>3</sub>N<sub>4</sub>(cr) have been discussed in Section X.1.1.2, where they are used to calculate the enthalpy of formation of ThN(cr). The selected value for the Gibbs energy of formation is:

$$\Delta_f G_m^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15 \text{ K}) = -(1200.1 \pm 15.7) \text{ kJ}\cdot\text{mol}^{-1}.$$

#### X.1.1.4 Th<sub>2</sub>N<sub>2</sub>O(cr)

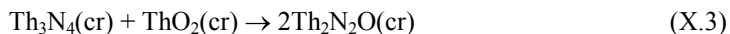
The oxynitride Th<sub>2</sub>N<sub>2</sub>O(cr) is now well characterised [1966BEN/ZAC]; it is hexagonal, space group  $R\bar{3}m$ , with  $a = (3.8833 \pm 0.0003) \text{ \AA}$ ,  $c = (6.1870 \pm 0.0003) \text{ \AA}$ . Juza and Gerke [1968JUZ/GER] give  $a = 3.880 \text{ \AA}$ ,  $c = 6.180$ , in general agreement with the more precise results of [1966BEN/ZAC], although such a precision should require an explicit indication of the temperature.

Kusakabe and Imoto [1971KUS/IMO], [1972KUS/IMO] have measured nitrogen pressures in the 'Th<sub>2</sub>N<sub>2</sub>O', 'ThO<sub>2</sub>', 'ThN' three-phase region from 1723 to 2258 K. However, mutual solubility among all these phases is appreciable at the higher temperatures. Benz [1967BEN] has suggested that there might be very considerable solubility between Th<sub>2</sub>N<sub>2</sub>O and Th<sub>3</sub>N<sub>4</sub>, although, subsequently [1972BEN], he showed that the mononitride phase in equilibrium with ThO<sub>2</sub> and Th<sub>2</sub>N<sub>2</sub>O contains rather little (< 0.02%) oxygen, even at 2000 K.

Moreover, combination of the nitrogen pressure measure by [1971KUS/IMO] for the reaction:



with the corresponding value for the Th<sub>3</sub>N<sub>4</sub>-ThN system, Reaction (X.1) gives for the all-solid reaction:



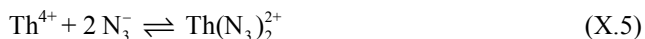
$$[\Delta_f G_m]_{1723\text{K}}^{2258\text{K}}(\text{X.3}) = -162348 + 70.156 T$$

This therefore corresponds to a highly negative entropy change for an all-solid reaction, and this in conjunction with the uncertainties in the formation of solid solutions in the solid phases, suggests that the reaction studied may not have been that given in (X.2), or there were other experimental errors in the study of this reaction. These data of [1971KUS/IMO] are therefore not considered further in this review.

Thus, no thermodynamic data for Th<sub>2</sub>N<sub>2</sub>O(cr) are selected.

#### X.1.2 Aqueous thorium azides

The only experimental study of chemical equilibria in the aqueous Th(IV)-azide system is a potentiometric investigation by Maggio *et al.* [1974MAG/ROM]. This investigation was made at 25°C in a 3.00 M NaClO<sub>4</sub> ionic medium, using potentiometric determination of the free hydrogen ion concentration. The equilibrium constants  $\log_{10} \beta_1$  (X.4) = (3.09 ± 0.11) and  $\log_{10} \beta_2$  (X.5) = (6.37 ± 0.08) refer to the following reactions:



These equilibrium constants were determined by a least-squares method and the uncertainty estimate is given at the  $3\sigma$  level. All experimental details are given in the publication and these values have been selected by the present review. In a previous publication Maggio *et al.* [1967MAG/ROM] have determined the equilibrium constant for the protonation of  $\text{N}_3^-$  under the same conditions as in [1974MAG/ROM] and report  $\log_{10} K(\text{X.6}) = 4.78$  for the reaction:



There is no error estimate in [1967MAG/ROM] and the uncertainty has therefore been estimated by this review to be  $\pm 0.03$ . There are a large number of determinations of  $\log_{10} K(\text{X.6})$  at different ionic strength, which have been used to calculate  $\log_{10} K^\circ(\text{X.6}) = (4.65 \pm 0.03)$  and the ionic interaction parameter  $\varepsilon(\text{N}_3^-, \text{Na}^+) = (0.015 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ ; the latter is the same as that estimated and selected in [2003GUI/FAN] but the uncertainty is five times smaller. The value of  $\log_{10} K^\circ$  is within the estimated uncertainty the same as that selected in [2003GUI/FAN],  $\log_{10} K^\circ(\text{X.6}) = (4.70 \pm 0.08)$ . This review has therefore not changed the previously selected value in [2003GUI/FAN]. Using the ion-interaction parameters selected in Appendix B and assuming  $\varepsilon(\text{ThN}_3^{3+}, \text{ClO}_4^-) = (0.55 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Th}(\text{N}_3)_2^{2+}, \text{ClO}_4^-) = (0.40 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ , this review has calculated the equilibrium constants at zero ionic strength:

$$\log_{10} \beta_1^\circ(\text{X.4}) = (4.44 \pm 0.64)$$

$$\log_{10} \beta_2^\circ(\text{X.5}) = (8.59 \pm 0.64)$$

where the uncertainty estimates also include the uncertainties in the interaction coefficients.

The selected Gibbs energy of formation calculated from the selected equilibrium constants and auxiliary data are:

$$\Delta_f G_m^\circ(\text{ThN}_3^{3+}, 298.15 \text{ K}) = -(381.93 \pm 6.74) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th}(\text{N}_3)_2^{2+}, 298.15 \text{ K}) = -(57.41 \pm 7.58) \text{ kJ}\cdot\text{mol}^{-1}.$$

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

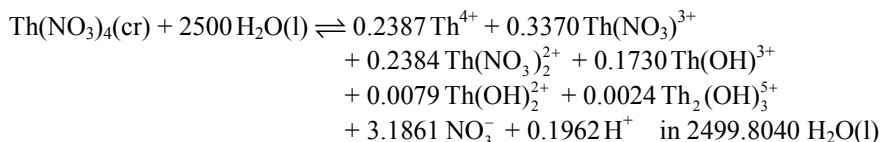
### X.1.3 Thorium nitrates

#### X.1.3.1 Solid thorium tetranitrates, $\text{Th}(\text{NO}_3)_4(\text{cr})$

Pure anhydrous thorium nitrate is difficult to prepare. It is obtained by thermal decomposition of an adduct resulting from the interaction of the tetrahydrate with dinitrogen pentoxide in anhydrous nitric acid [1955FER/KAT]. Other preparative routes involving dinitrogen tetroxide have also been explored [1965SCH/KOE], [1984KUM/TUC].

The properties of this compound have not been extensively studied. Its enthalpy of solution ( $\text{H}_2\text{O}/\text{Th}$  molar ratio = 2500) was reported without details by Ferraro *et al.* [1956FER/KAT] to be  $-(145.2 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ , the uncertainty being estimated by this review.

As discussed in Appendix A, the dissolution reaction can be written as:



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 (neither for thorium nor for uranium), we will not attempt to use further the experimental results of [1956FER/KAT] which are given here for information only.

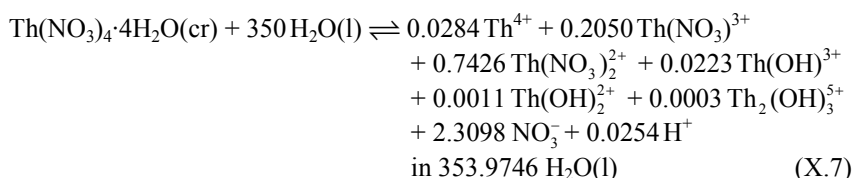
### X.1.3.2 Thorium tetranitrate hydrates

Although various hydrates have been described in the literature, Ferraro *et al.* [1954FER/KAT] showed that only the penta- and tetrahydrate could be obtained from the  $\text{Th}(\text{NO}_3)_4\text{-HNO}_3\text{-H}_2\text{O}$  system. Brown, in the most recent Gmelin supplement [1987BRO], gives a ternary phase diagram for this system.  $\text{Th}(\text{NO}_3)_4\cdot 5\text{H}_2\text{O}(\text{cr})$  is the phase in equilibrium with the saturated solution at 298.15 K.

Both these hydrates have been studied crystallographically. The tetrahydrate is reported by Charpin *et al.* [1987CHA/CHE] to be monoclinic, space group  $P2_1/n$ , with  $a = (7.438 \pm 0.001) \text{ \AA}$ ,  $b = (17.530 \pm 0.008) \text{ \AA}$ ,  $c = (9.183 \pm 0.001) \text{ \AA}$ , and  $\beta = (99.72 \pm 0.01)^\circ$  based on X-ray diffraction studies on single crystals. The pentahydrate is orthorhombic, space group  $Fdd2$ , and two groups of authors give lattice parameters in agreement:  $a = (11.182 \pm 0.003) \text{ \AA}$ ,  $b = (22.873 \pm 0.005) \text{ \AA}$ , and  $c = (10.573 \pm 0.003) \text{ \AA}$ , according to Ueki *et al.* [1966UEK/ZAL], from X-ray diffraction studies, and:  $a = (11.191 \pm 0.007) \text{ \AA}$ ,  $b = (22.889 \pm 0.015) \text{ \AA}$ , and  $c = (10.579 \pm 0.007) \text{ \AA}$ , according to Taylor *et al.* [1966TAY/MUE] from neutron diffraction data.

The enthalpy of solution of the tetrahydrate in  $350\text{H}_2\text{O}$  was reported without details by Ferraro *et al.* [1956FER/KAT] as  $-(32.01 \pm 1.70) \text{ kJ}\cdot\text{mol}^{-1}$ , the uncertainty being that estimated by this review.

The dissolution reaction can be written as:



As in the case of the dissolution of the anhydrous thorium nitrate in water by the same authors, these results cannot be used as such for the determination of the enthalpy of formation of the compound, due to the lack of experimental data on the enthalpies of formation of the thorium nitrate complexes. This is also the case for the enthalpy of solution of the pentahydrate in water to reach the same final concentration, also given by the same authors as  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(14.85 \pm 1.70) \text{ kJ}\cdot\text{mol}^{-1}$ . However, as discussed below, the difference between the enthalpies of solution of the pentahydrate and the tetrahydrate in the same medium,  $-(17.16 \pm 2.40) \text{ kJ}\cdot\text{mol}^{-1}$ , reported by these authors has been used to obtain  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$ .

Morss and McCue [1976MOR/MCC] measured the enthalpy of solution of high purity  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}(\text{cr})$  in 0.01 M  $\text{HClO}_4$  at 293.15, 298.15, and 308.15 K. At infinite dilution, and after a small correction for hydrolysis, the value  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(19.807 \pm 0.250) \text{ kJ}\cdot\text{mol}^{-1}$ , was reported. The uncertainty in this value is estimated by the present review.

Use of  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}^{4+}, 298.15 \text{ K}) = -(768.7 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = -(285.83 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NO}_3^-, \text{aq}, 298.15 \text{ K}) = -(206.85 \pm 0.40) \text{ kJ}\cdot\text{mol}^{-1}$  leads to

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(3005.4 \pm 2.8) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

The enthalpy of formation of the tetrahydrate can be calculated from this value, together with the difference between the enthalpies of solution of the pentahydrate and the tetrahydrate in 350 mol  $\text{H}_2\text{O}$  by [1956FER/KAT],  $-(17.16 \pm 0.40) \text{ kJ}\cdot\text{mol}^{-1}$ , and the partial molar enthalpy of formation of water in the resulting solution. There are insufficient data to calculate the latter precisely, but in such a dilute solution (*ca.* 0.15 m) it will differ very little from  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K})$ , so we have taken  $\Delta_{\text{f}}H_{\text{m}}(\text{H}_2\text{O}, \text{partial}, 298.15 \text{ K}) = -(285.83 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$  with increased uncertainty limits. This gives

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(2702.4 \pm 3.8) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

The heat capacity of the pentahydrate has been measured by Cheda *et al.* [1976CHE/WES]. Their results,

$$C_{\text{p,m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (480.7 \pm 0.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (543.1 \pm 0.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

are selected in this review, but with increased uncertainty limits. The entropy of this compound has been used in this review for the evaluation of:



$$S_m^\circ(\text{Th}^{4+}, 298.15 \text{ K}) = -(423.1 \pm 16.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

–see Section VI.1.

The Gibbs energy of formation is calculated to be:

$$\Delta_f G_m^\circ(\text{Th}(\text{NO}_3)_4\cdot 5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(2322.7 \pm 2.8) \text{ kJ}\cdot\text{mol}^{-1}.$$

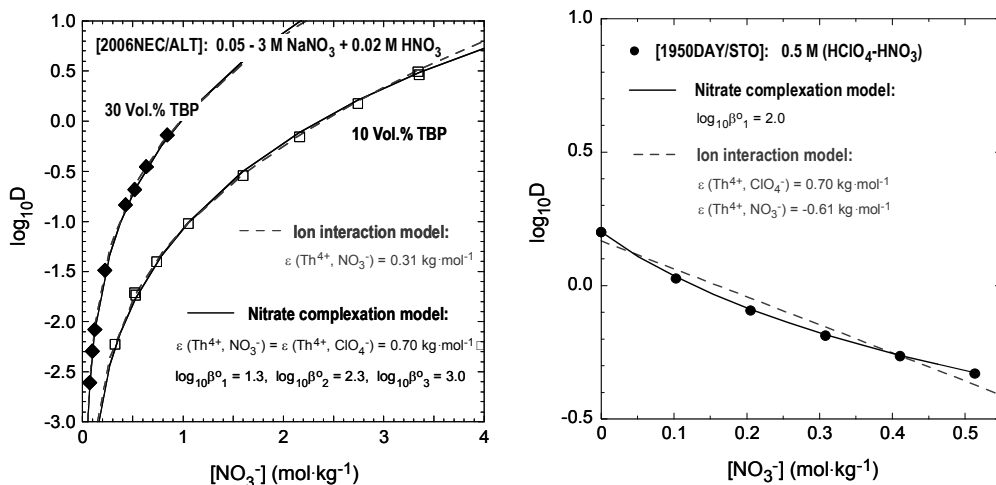
As mentioned in the discussion of the results of [1976MOR/MCC] in Section VI.1 and in Appendix A, the solubility of the pentahydrate in water at 298.15 K has been measured by Appelblatt *et al.* [1973APE/AZO] as  $3.74 \text{ mol}\cdot\text{kg}^{-1}$  and by [1976MOR/MCC] as  $3.66 \text{ mol}\cdot\text{kg}^{-1}$ . As noted, the selected value is  $(3.7 \pm 0.1) \text{ mol}\cdot\text{kg}^{-1}$ .

Vapour pressure measurements of thorium nitrate solutions have been reported by Robinson and Levien [1947ROB/LEV] and by Appelblatt *et al.* [1973APE/AZO2]. Enthalpies of dilution and vapour pressure data on thorium nitrate solutions have been correlated by Fricke [1929FRI2]. Lange and Miederer [1957LAN/MIE] have also reported enthalpies of dilution.

### X.1.3.3 Aqueous thorium nitrates

The available information on chemical equilibria in the Th(IV)-nitrate system, [1950DAY/STO], [1951ZEB/ALT], [1956FOM/MAI], [1960DAN], [1968TED/RUM], [1976SOU/SHA] and [2006NEC/ALT] indicates that the complexes formed are weak and we have then the general problem already mentioned to decide if the systems should be treated using a complex formation or an ion-interaction model. For reasons given in the following text and in Appendix A for [2006NEC/ALT], only the equilibrium constants in that paper have been accepted by this review. As in the case of the chloride complexes, this review has re-evaluated the experimental TBP extraction study of [2006NEC/ALT] in aqueous nitrate media ( $0.05\text{--}3 \text{ M NaNO}_3 + 0.02 \text{ M HNO}_3$ ) and the TTA extraction study of [1950DAY/STO] in  $0.5 \text{ M HClO}_4\text{-HNO}_3$  and found that both approaches describe the experimental observations with about the same accuracy (Figure X-1). However, the value of  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-)$  calculated from the data of [1950DAY/STO] in  $0.5 \text{ M HClO}_4\text{-HNO}_3$  is  $-0.61 \text{ kg}\cdot\text{mol}^{-1}$ . This review finds this value unlikely; such a large negative value would indicate the presence of strong ion-ion interactions, *cf.* the discussion on  $\varepsilon(\text{Th}^{4+}, \text{BrO}_3^-)$ , and suggests that the data in [1950DAY/STO] are affected by unidentified systematic errors; these data have therefore not been accepted by the review. The value  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = -0.61 \text{ kg}\cdot\text{mol}^{-1}$  is very different from  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$  determined by [2006NEC/ALT] in a study accepted by this review.

Figure X-1: Experimental distribution coefficients of Th(IV) in the TBP extraction study of [2006NEC/ALT] (aqueous phase: 0.05–3 M NaNO<sub>3</sub> + 0.02 M HNO<sub>3</sub>, 22°C) and the TTA extraction study of [1950DAY/STO] (aqueous phase: 0.5 M H(ClO<sub>4</sub>-NO<sub>3</sub>), 25°C) and data evaluation using both the ion interaction model (dashed lines) and the nitrate complexation model (solid lines).



To remain consistent with previous volumes in the series of "Chemical Thermodynamics", the present review continues to use the complex formation model. This choice has support from the results of large-angle X-ray diffraction studies of aqueous solution that clearly demonstrate chemical bonding of NO<sub>3</sub><sup>-</sup> to Th(IV) in hydroxide complexes [1968JOH2] and [1991JOH/MAG]. Figure VII-4 shows the coordination around Th from a single crystal X-ray diffraction study of a basic thorium nitrate compound [1968JOH].

In the corresponding U(IV)-nitrate system one observes a change in the UV/Vis absorption spectrum of the U<sup>4+</sup> ion on addition of nitrate, an observation that is difficult to reconcile with the ion-interaction model. As the chemistry of Th(IV) and U(IV) is very similar we have additional support for the complex formation model:



When using this model the interaction coefficient of Th<sup>4+</sup> in nitrate solution is set equal to the value in non-complexing perchlorate solution  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ . The  $\Delta\varepsilon_n(\text{X.8})$  values from the analogous reactions of U(IV),  $\Delta\varepsilon(n=1) = -(0.21 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  and  $\Delta\varepsilon(n=2) = -(0.41 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$  in HNO<sub>3</sub> media and  $\Delta\varepsilon(n=1) = -(0.10 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$  and  $\Delta\varepsilon(n=2) = -(0.19 \pm 0.16) \text{ kg}\cdot\text{mol}^{-1}$  in NaNO<sub>3</sub> media [1992GRE/FUG], are used for ionic strength corrections. The experimental data in [1960DAN] have been obtained by measuring the

distribution of trace amounts of Th(IV) between a nitrate loaded anion exchanger and test solutions with nitrate concentrations varying between 1.56 and 8.44 M. These data indicate the formation of an uncharged complex  $\text{Th}(\text{NO}_3)_4(\text{aq})$  and of anionic species  $\text{Th}(\text{NO}_3)_5^-$  and  $\text{Th}(\text{NO}_3)_6^-$  but the reported equilibrium constants are not accepted by this review for reasons given in Appendix A. The experimental data from [1968TED/RUM] have been obtained using cation exchange in a 2.00 M  $\text{H}^+(\text{NO}_3^-, \text{ClO}_4^-)$  ionic medium; they report the formation of three nitrate complexes  $\text{Th}(\text{NO}_3)_n^{4-n}$ ,  $n = 1-3$ . The experimental method and the analysis of the data seem satisfactory, but the reported values for the equilibrium constants seem too large, *cf.* Appendix A and have therefore not been accepted by this review. The data from [1976SOU/SHA] have also been obtained using cation exchange, but in test solutions where the ionic strength varies and are therefore not used by this review. Recalculation of the equilibrium constant from [1950DAY/STO],  $\log_{10} \beta_1$  (X.8) = 0.67 at 25°C and an ionic strength of 0.50 M  $\text{H}(\text{ClO}_4, \text{NO}_3)$ , gives  $\log_{10} \beta_1^\circ = 1.97$ , significantly larger than the corresponding value for the formation of  $\text{U}(\text{NO}_3)_3^{3+}$ ,  $\log_{10} \beta_1^\circ = (1.47 \pm 0.13)$  that is based on several different experimental determinations. The stability of actinide complexes in a given oxidation state is in general smaller for thorium complexes than for other actinides; the value from [1950DAY/STO] is larger than that for U(IV), another reason why it is not accepted. The values recalculated from the study of [2006NEC/ALT],  $\log_{10} \beta_1^\circ = (1.3 \pm 0.2)$  and  $\log_{10} \beta_2^\circ = (2.3 \pm 0.4)$ , in combination with  $\log_{10} \beta_3^\circ = (3.0 \pm 0.5)$  derived with an estimated SIT coefficient of  $\varepsilon(\text{Th}(\text{NO}_3)_3^+, \text{ClO}_4^-) = (0.25 \pm 0.15) \text{ kg} \cdot \text{mol}^{-1}$ , are close to the corresponding values for the analogous U(IV) nitrate complexes (*cf.* Table X-1). In particular  $\log_{10} \beta_1^\circ(\text{Th}(\text{NO}_3)_3^{3+})$  fits well into the series of the formation constants selected in previous NEA-TDB reviews for the nitrate complexes of tetravalent actinides;  $\log_{10} \beta^\circ$  values of analogous complexes usually increase from Th(IV) to Pu(IV).

Table X-1: Formation constants of An(IV) nitrate complexes at  $I = 0$  and 25°C.

An(IV)	$\log_{10} \beta_1^\circ$	$\log_{10} \beta_2^\circ$	$\log_{10} \beta_3^\circ$	Reference
Th(IV)	1.97 <sup>(a)</sup>			Recalculated from [1950DAY/STO]
	$1.67 \pm 0.84$	$2.25 \pm 1.34$		Recalculated from [1951ZEB/ALT]
	$2.19 \pm 0.38$ <sup>(a)</sup>	$3.41 \pm 0.46$ <sup>(a)</sup>	$3.64 \pm 0.41$ <sup>(a)</sup>	Recalculated from [1956FOM/MAI]
	$2.59 \pm 0.37$ <sup>(a)</sup>	$3.83 \pm 0.49$ <sup>(a)</sup>	$3.74 \pm 0.50$ <sup>(a)</sup>	Recalculated from [1968TED/RUM]
	$1.3 \pm 0.2$	$2.3 \pm 0.4$	$3.0 \pm 0.5$	Recalculated from [2006NEC/ALT]
U(IV)	$1.47 \pm 0.13$	$2.30 \pm 0.35$	<sup>(b)</sup>	[1992GRE/FUG]
Np(IV)	$1.90 \pm 0.15$			[2001LEM/FUG]
Pu(IV)	$1.95 \pm 0.15$			[2001LEM/FUG]

a: Not accepted by this review.

b: The evidence for the formation of  $\text{U}(\text{NO}_3)_3^+$  at higher nitrate concentration was discussed in [1992GRE/FUG] but the reported literature values of  $\log_{10} \beta_3$  in 2.0–3.5 M  $\text{H}(\text{ClO}_4\text{-NO}_3)$  were not accepted.

Using liquid-liquid extraction with TTA as extractant, Zebroski *et al.* [1951ZEB/ALT] derived formation constants of  $\beta_1 = 2.83 \text{ M}^{-1}$  and  $\beta_2 = 1.91 \text{ M}^{-2}$  in a 5.97 M  $\text{Na}(\text{NO}_3, \text{ClO}_4)$  ionic medium with nitrate concentrations up to 4.93 M. Because of the high ionic strength ( $I_m = 8.4 \text{ mol}\cdot\text{kg}^{-1}$ ) the values extrapolated to  $I = 0$  with the SIT have very large uncertainties (*cf.* Table X-1). Fomin and Maiorova [1956FOM/MAI] suggest the formation of the complexes  $\text{Th}(\text{NO}_3)_n^{4-n}$ ,  $n = 1-4$ , in 2.00 M  $\text{H}(\text{NO}_3, \text{ClO}_4)$ , with a chemical model based on only five different nitrate concentrations. However, the liquid-liquid two-phase system used by [1956FOM/MAI] (Th extraction with TBP from aqueous  $\text{HClO}_4\text{-HNO}_3$  mixtures) is not appropriate for studying the thorium nitrate complexation because the composition of the thorium complexes extracted into the organic phase varies with the  $\text{ClO}_4^-/\text{NO}_3^-$  ratio in the aqueous phase. The calculated formation constants are considerably overestimated. Using the value of  $\log_{10} \beta_1 = (0.78 \pm 0.04)$  calculated in [1956FOM/MAI] and the SIT with  $\Delta\varepsilon(n = 1) = -0.21 \text{ kg}\cdot\text{mol}^{-1}$  this review obtains  $\log_{10} \beta_1^\circ = 2.19$ , which differs considerably from the corresponding values for other actinides, *cf.* Table X-1. This review has therefore not accepted the equilibrium constants proposed by Fomin and Maiorova. Peppard *et al.* [1962PEP/NAM] have made a detailed study of extraction equilibria in the toluene-Th(IV)- $\text{Cl}^-$ - $\text{NO}_3^-$  system. However, there is no quantitative information on complex formation equilibria with nitrate.

Despite the few experimental data for the Th(IV)-nitrate system, this review has selected the equilibrium constants:

$$\log_{10} \beta_1^\circ = (1.3 \pm 0.2)$$

$$\log_{10} \beta_2^\circ = (2.3 \pm 0.4)$$

based on the data from [2006NEC/ALT] as described in Appendix A. This choice is supported by the good agreement with the corresponding data for the U(IV)-nitrate system.

It has to be emphasised that these equilibrium constants must not be combined with  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = (0.31 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$  used in the Sections VII.3 and VIII.1.2 on aqueous thorium hydroxide and fluoride complexes; this value refers to a strict ion interaction approach where the effect of nitrate complexation is included in the interaction coefficient. The equilibrium constants for the formation of nitrate complexes must be combined with  $\varepsilon(\text{Th}^{4+}, \text{NO}_3^-) = \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{Th}(\text{NO}_3)_3^{3+}, \text{NO}_3^-) = \varepsilon(\text{Th}(\text{NO}_3)_3^{3+}, \text{ClO}_4^-) = (0.56 \pm 0.14) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{Th}(\text{NO}_3)_2^{2+}, \text{NO}_3^-) = \varepsilon(\text{Th}(\text{NO}_3)_2^{2+}, \text{ClO}_4^-) = (0.43 \pm 0.18) \text{ kg}\cdot\text{mol}^{-1}$ , and  $\varepsilon(\text{Th}(\text{NO}_3)_3^+, \text{NO}_3^-) = \varepsilon(\text{Th}(\text{NO}_3)_3^+, \text{ClO}_4^-) = (0.25 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ . The selected equilibrium constants yield:

$$\Delta_f G_m^\circ(\text{Th}(\text{NO}_3)_3^{3+}, 298.15 \text{ K}) = -(823.0 \pm 5.4) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th}(\text{NO}_3)_2^{2+}, 298.15 \text{ K}) = -(939.5 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1}$$

### X.1.4 Thorium nitrite complexes

There are no experimental studies reported of Th(IV) nitrite complexes in aqueous solution, only an investigation in methanol [1968GOL/KAL] that reports the formation of the ternary complexes  $\text{Th}(\text{OMe})_2\text{NO}_2^+$ ,  $\text{Th}(\text{OMe})_2(\text{NO}_2)_2$  and  $\text{Th}(\text{OMe})_2(\text{NO}_2)_3^-$  and their equilibrium constants. However, this information cannot be used to make estimates of the composition and equilibrium constants of nitrite complexes in aqueous solution. As the nitrite ion is a much stronger base than nitrate ion, one may however expect the Th(IV) nitrite complexes to be stronger than the corresponding nitrate complexes.

## X.2 Phosphorus compounds and complexes

### X.2.1 Solid and gaseous thorium phosphides

There are only two solid thorium phosphides, ThP(cr) and Th<sub>3</sub>P<sub>4</sub>(cr), and little thermodynamic information is available on either of these.

#### X.2.1.1 Thorium monophosphide ThP(cr)

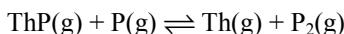
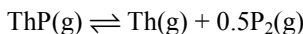
ThP(cr) has the fcc NaCl structure, isomorphous with most of the lower actinide MX(cr) compounds, (X = N, S, P). It was initially thought to have a considerable range of homogeneity [1965GIN/WIL], but in a detailed study of the Th-ThP subsystem, Javorsky and Benz [1967JAV/BEN] showed that the lower phase boundary is at *ca.* ThP<sub>0.98</sub> over most of its range of stability. The upper phase boundary has still not been established.

The lattice parameter of the stoichiometric phase was found to be  $(5.833 \pm 0.001)$  Å after long anneals at 1523 and 1073 K [1967JAV/BEN]. These authors also determined the (congruent) melting point of  $(3263 \pm 60)$  K, slightly higher than the 'apparent' melting point in helium gas given by Baskin [1969BAS], 3173 K, but the latter author was unable to determine whether this was the true melting point, or the temperature of a eutectic with the tungsten container. The higher value is preferred.

Maurice *et al.* [1979MAU/BOU] have measured the heat capacity of ThP(cr) from 2 to 15 K, but there are no other heat capacity data above this temperature. Rand [1975RAN] estimated the entropy of ThP(cr) by a comparison of the entropies of thorium and uranium compounds of nitrogen, sulphur and phosphorus, as  $S_m^\circ(\text{ThP, cr, 298.15 K}) = (70.3 \pm 4.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The corresponding enthalpy of formation was calculated by the same author from the combined measurements of the emf study by [1966GIN/ARO] and the mass spectrometric study by [1963GIN/EFI] as  $\Delta_f H_m^\circ(\text{ThP, cr, 298.15 K}) = (347 \pm 42) \text{ kJ}\cdot\text{mol}^{-1}$ . As noted below and in Appendix A, there are some doubts about the validity of the data obtained in the latter study, and these values are given for information only.

**X.2.1.2 Gaseous thorium phosphide ThP(g)**

Gingerich [1968GIN], [1969GIN2] has made two mass-spectrometric determinations of the pressures of ThP(g) existing over Th-B-P alloys at four temperatures between 2702 and 2804 K and gave partial pressures of the species in the three equilibria:



Gingerich [1969GIN] further estimated molecular parameters for ThP(g) by established spectroscopic approximations. We have repeated these calculations, using these estimates, and used third-law calculations to derive average values of  $\Delta_f H_m^\circ$  (ThP, g, 298.15 K) = (537 ± 8), (551 ± 8), and (547 ± 6) kJ·mol<sup>-1</sup> from the three reactions, with  $S_m^\circ$  (ThP, g, 298.15 K) = (276.6 ± 10.0) J·K<sup>-1</sup>·mol<sup>-1</sup>. The auxiliary data for P(g) and P<sub>2</sub>(g) were taken from Table IV-1 and [1989COX/WAG]. This indicates a value of  $\Delta_f H_m^\circ$  (ThP, g, 298.15 K) = (545 ± 30) kJ·mol<sup>-1</sup>, where the increased uncertainty includes those in the experimentation and the estimates of the thermal functions for ThP(g). This value shows that ThP(g) is always a quite minor species in the vaporisation of ThP, and in view of this and the paucity of the experimental data, the above values are given for information only, as for ThN(g).

**X.2.1.3 Th<sub>3</sub>P<sub>4</sub>(cr)**

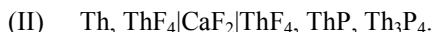
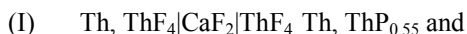
Th<sub>3</sub>P<sub>4</sub>(cr) has a bcc structure, space group  $I\bar{4}3d$ , isomorphous with many of the actinide compounds with the same stoichiometry, except the nitrides. Indeed, it was the first of the group of compounds with this structure to be characterised. The lattice parameter of Th<sub>3</sub>P<sub>4</sub> determined by various authors from samples obtained by various procedures involving direct reaction of the elements or of their hydrides varies over a range of 0.05 Å [1983WED]. We will only cite here the most precise result of Price and Warren [1965PRI/WAR] who report  $a = (8.6530 \pm 0.0005)$  Å, for samples obtained from high purity analysed thorium metal.

Rand [1975RAN] estimated the entropy and enthalpy of formation of Th<sub>3</sub>P<sub>4</sub>(cr) with that of the monophosphide (see Section X.2.1.1) as  $S_m^\circ$  (Th<sub>3</sub>P<sub>4</sub>, cr, 298.15 K) = (246.8 ± 12.6) J·K<sup>-1</sup>·mol<sup>-1</sup> and  $\Delta_f H_m^\circ$  (Th<sub>3</sub>P<sub>4</sub>, cr, 298.15 K) = (1146 ± 126) kJ·mol<sup>-1</sup>. As noted immediately below and in Appendix A, there are some doubts about the validity of some of the data employed and these values are given for information only.

There are two complementary measurements of the thorium and phosphorus potentials in this system. Gingerich and Efimenko [1963GIN/EFI] have measured mass-spectrometrically the pressures of the phosphorus species over thorium phosphides from ThP<sub>0.63</sub>(cr) to ThP<sub>1.27</sub>(cr) in the range 1131 to 2243 K, while Gingerich and Aronson [1966GIN/ARO] have measured the thorium activities in the {Th(cr) (saturated with P) + ThP<sub>1-x</sub>(cr)} and {ThP<sub>1+x</sub>(cr) + Th<sub>3</sub>P<sub>4</sub>(cr)} diphasic regions from 1073 to 1223 K using

solid-state electrochemical cells with a  $\text{CaF}_2(\text{cr})$  electrolyte. However, as noted in Appendix A, there are several indications that equilibrium was not attained in the mass-spectrometric study [1963GIN/EFI], even at the highest temperatures, and these data are not used in this review.

Gingerich and Aronson [1966GIN/ARO] employed two cells:



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. The ThP samples contained up to 2 mol% oxygen, so these results presumably refer to oxygen-saturated ThP(cr). More details are given in Appendix A.

The standard deviation of the emf cell (II) at the mid-temperature was estimated to be as much 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:



to be

$$[\Delta_f G_m]_{1073\text{K}}^{1223\text{K}}((\text{X.9}), T) = -(224700 \pm 23400) + (38.9 \pm 31.0) T \quad \text{J}\cdot\text{mol}^{-1}$$

where the uncertainties are twice those quoted by the authors.

In the absence of any other selected thermodynamic data for the thorium phosphides, no further processing of these results can be attempted.

## X.2.2 Solid thorium hypophosphites and phosphites

Many thorium hypophosphites, phosphites, their hydrates and related compounds with monovalent cations (usually  $\text{K}^+$ ) have been mentioned in the literature (see the Gmelin review by Bickel [1993BIC]), but the information available is essentially limited to preparation procedures, analysis, vibrational spectra and some DTA studies. X-ray structures have not been reported and, in fact, many of these compounds are amorphous to X-rays. Since no thermodynamic data relevant to this review have been reported, these compounds are not considered further.

## X.2.3 Thorium phosphate compounds and complexes

### X.2.3.1 Solid thorium phosphates

On the basis of X-ray diffraction and thermogravimetric data, Burdese and Borlera [1963BUR/BOR] presented a phase diagram for the system  $\text{P}_2\text{O}_5\text{-ThO}_2$ , in which they

identified five compounds:  $\text{Th}(\text{PO}_3)_4$ ,  $\text{ThP}_2\text{O}_7$ ,  $\text{Th}_3(\text{PO}_4)_4$ ,  $(\text{ThO})_2\text{P}_2\text{O}_7$ , and  $(\text{ThO})_3(\text{PO}_4)_2$ . Structural information (see Table X-2) are given for the first three compounds but not for the oxysalts  $(\text{ThO})_2\text{P}_2\text{O}_7$ , and  $(\text{ThO})_3(\text{PO}_4)_2$  which are reported to form above 1423 K.

Table X-2: Structural data for thorium phosphates.

Phase	Symmetry	Space Group	Lattice parameters (Å)	Reference
$\alpha\text{-Th}(\text{PO}_3)_4$ (< 1023 K)	orthorhombic		$a = 14.35$	[1963BUR/BOR]
			$b = 15.11$	
			$c = 9.05$	
			$a = 6.947 \pm 0.004$	[1972MAS/GRE] <sup>a</sup>
			$b = 15.120 \pm 0.020$	
			$c = 9.069 \pm 0.007$	
$\text{Th}(\text{PO}_3)_4$	tetragonal		$a = 11.440 \pm 0.010$	[1972MAS/GRE]
			$c = 14.978 \pm 0.020$	
$\text{Th}(\text{PO}_3)_4$	triclinic		$a = 15.51 \pm 0.015$	[1972MAS/GRE] <sup>b</sup>
			$b = 8.251 \pm 0.007$	
			$c = 8.796 \pm 0.008$	
			$\alpha = 117.80 \pm 0.70^\circ$	
			$\beta = 112.32 \pm 0.50^\circ$	
			$\gamma = 89.14 \pm 0.05^\circ$	
$\text{Th}_3(\text{PO}_4)_4$	monoclinic		$a = 10.55$	[1963BUR/BOR]
			$b = 10.66$	
			$c = 8.80$	
			$\beta = 106.68^\circ$	
$\alpha\text{-ThP}_2\text{O}_7$ (< 1083 K)	cubic		$a = 8.721 \pm 0.006$	[1963BUR/BOR2]
$\beta\text{-ThP}_2\text{O}_7$ (> 1083 K)	orthorhombic		$a = 11.620 \pm 0.007$	[1963BUR/BOR2] <sup>c</sup>
			$b = 12.80 \pm 0.01$	
			$c = 7.121 \pm 0.004$	
$\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$	orthorhombic	<i>Pcam</i>	$a = 12.8646 \pm 0.0009$	[1996BEN/BRA]
			$b = 10.4374 \pm 0.0008$	
			$c = 7.0676 \pm 0.0005$	

a: Apparent cell, based on extended exposures; the authors propose also a real cell with doubled  $a$  and  $b$  parameters.

b: Primitive cell with 4  $\text{Th}(\text{PO}_3)_4$  units deduced for an A-face-centred cell with 8 formula units.

c: Values in agreement with the less precise values reported by the same authors in [1963BUR/BOR].

For the metaphosphate  $\text{Th}(\text{PO}_3)_4$ , Burdese and Borlera [1963BUR/BOR] indicate an orthorhombic structure stable up to 1023 K. However, for the same compound, Masse and Grenier [1972MAS/GRE] (see Table X-2) found three structures (ortho-



rhombic, tetragonal and monoclinic), in three different crystals selected from the same preparation, but with no indication of the temperature range in which they are stable. The lattice parameters reported by [1972MAS/GRE] for the orthorhombic structure do not correspond to those given by [1963BUR/BOR]. Masse and Grenier [1972MAS/GRE] also indicate an alternative method of preparation of the monoclinic form. The structure of thorium orthophosphate,  $\text{Th}_3(\text{PO}_4)_4$  was characterised as monoclinic by [1963BUR/BOR].

More recently, in the framework of broad studies on the potentialities of phosphate matrices for radioactive waste storage, different compounds ( $\text{Th}_2(\text{PO}_4)_2 \cdot \text{HPO}_4 \cdot \text{H}_2\text{O}$ ;  $\text{ThOHPO}_4$ ; and Th-phosphates containing F,  $\text{SO}_4$ , Cs, or Ba) have been synthesised from aqueous solutions ([2000THO/DAC], [2001BRA/DAC2], [2002BRA/DAC]). Since no thermodynamic data relevant to the review have been reported, these compounds are not considered further. Also, in this context of radioactive waste disposal, Bénard *et al.* [1996BEN/BRA] characterised  $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ , thorium phosphate diphosphate (TPD), the synthesis of which has been summarised in [2001BRA/DAC]. The TPD structure was determined by [1996BEN/BRA] as orthorhombic, space group *Pcam*, from powder and single crystal X-ray diffraction (see Table X-2). Infra-red spectroscopy measurements confirmed the presence of  $\text{P}_2\text{O}_7$  entities in the compound. This result and further studies by the same group, in particular in [1998BRA/DAC], led the authors to cast doubt about the conditions of preparation and identification of various phosphates and related compounds (including  $\text{Th}_3(\text{PO}_4)_4$ ) described in the earlier literature. The thermal diffusivity, thermal conductivity and specific heat of TPD were reported by Dacheux *et al.* [2002DAC/CHA] between room temperature and 1273 K.

The equation for the fit to  $C_p$  in the text of [2002DAC/CHA] seems to be in error, and we have refitted their results for the specific heat to the relation:

$$C_p = 0.46262 + 6.94205 \times 10^{-5} T - 1.2367 \times 10^{-10} T^2 - 9402.0 T^{-2} \text{ (J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}\text{)}$$

which for a molecular weight of 1505.981 corresponds to the molar heat capacity equation:

$$[C_{p,m}^\circ]_{298.15\text{K}}^{1273\text{K}} = 696.70 + 0.10455 T - 1.8625 \times 10^{-7} T^2 - 1.4159 \times 10^7 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The calculated value of the heat capacity at 298.15 K is thus

$$C_{p,m}^\circ(\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7, \text{cr}, 298.15 \text{ K}) = (569 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

which is the selected value, with an uncertainty estimated by the review.

The only thermochemical values on the phosphate compounds reported above have been deduced from solubility measurements and are discussed in the Section X.2.3.2.

### X.2.3.1.1 Solid thorium phosphate hydrates

The preparation and a number of properties of numerous hydrates of thorium phosphate and of acid and basic phosphates, as well as some of their properties, have been described in the literature – see the review in the Gmelin Handbook [1993BIC], which also includes a survey of ternary phosphates (and their hydrates) with a number of cations. Some of these compounds have been studied in relation with the determination of phosphate complexes in solution and are discussed in the relevant Section X.2.3.2.

### X.2.3.1.2 Solid thorium hypophosphate

The compound  $\text{ThP}_2\text{O}_6 \cdot 11\text{H}_2\text{O}$  was reported more than a century ago [1899KAU]. It has subsequently attracted attention for its low solubility in moderately concentrated hydrochloric acid and was recommended for removing thorium from its admixtures with the rare earth elements ([1948MOE/SCH] and references therein). The water content appears quite dependent of the mode of preparation; for instance, [1953MOE/QUI] report a mode of preparation leading to the dihydrate which, although not gelatinous like the more hydrated species, still appears non-crystalline by X-ray diffraction. Moeller and Quinty [1952MOE/QUI] describe the synthesis of  $\text{ThP}_2\text{O}_6(\text{s})$  with an unspecified water content and determined its solubility in 1–6 M hydrochloric acid ( $[\text{Th}] = 2.5 \times 10^{-5}$  M in 1 M HCl), demonstrating that this solid phase is sparingly soluble. There are no other thermodynamic data reported for this compound.

### X.2.3.2 Aqueous complexes with phosphate ions

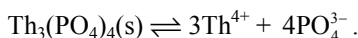
The chemical reactions in the aqueous Th(IV)-phosphate system have been investigated experimentally using liquid-liquid distribution and solubility measurements; in addition there are a number of qualitative studies that do not provide thermodynamic data. The most precise studies have been made using liquid-liquid distribution; Zebrowski *et al.* [1951ZEB/ALT] using thenoyltrifluoroacetone (TTA) and Elyaoui *et al.* [1990ELY/BRI] using di(2-ethylhexyl)phosphoric acid (HDEHP) as extracting ligands. The first study [1951ZEB/ALT] was made at a constant ionic strength of 2.00 M  $(\text{Na,H})\text{ClO}_4$  in test solutions at four different and constant hydrogen ion concentrations, 0.25, 0.50, 1.00 and 2.00 M that allowed a proper determination of the stoichiometry of the ternary complexes  $\text{ThH}_p(\text{PO}_4)_q^{(4+p-3q)}$ . The latter study [1990ELY/BRI] was made at an ionic strength of 0.200 M in the pH range 0.7–3.5 and at phosphoric acid concentrations up to 1.0 M. Elyaoui *et al.* used “electrostatic considerations” to suggest the stoichiometry listed in Table X-3. The proposed stoichiometry of the complexes is very different from those proposed in [1951ZEB/ALT] and the constants of [1990ELY/BRI] have not been accepted by this review.

Table X-3: Equilibrium constants for complexes formed in the Th(IV)-phosphate system at 25°C and an ionic strength of 0.20 M from [1990ELY/BRI]. The first column contains the stoichiometry as deduced from the experimental liquid-liquid distribution data and the last column the stoichiometry proposed using electrostatic considerations.  $H_{L_n}$  denotes the number of protons formed in the reaction, but not their origin.

Experimental stoichiometry of the complexes in [1990ELY/BRI]	Equilibrium constant, $\log_{10} K$	Proposed stoichiometry of the complexes in [1990ELY/BRI]
$\text{ThH}_{-2}(\text{H}_3\text{PO}_4)^{2+}$	$5.22 \pm 0.04$	$\text{Th}(\text{OH})(\text{H}_2\text{PO}_4)^{2+}$
$\text{ThH}_{-3}(\text{H}_3\text{PO}_4)^+$	$3.62 \pm 0.04$	$\text{Th}(\text{OH})_2(\text{H}_2\text{PO}_4)^+$
$\text{ThH}_{-1}(\text{H}_3\text{PO}_4)^{3+}$	$5.65 \pm 0.05$	$\text{Th}(\text{H}_2\text{PO}_4)^{3+}$
$\text{ThH}_{-3}(\text{H}_3\text{PO}_4)_2^+$	$4.70 \pm 0.04$	$\text{Th}(\text{OH})(\text{H}_2\text{PO}_4)_2^+$
$\text{ThH}_{-4}(\text{H}_3\text{PO}_4)_3(\text{aq})$	$2.90 \pm 0.04$	$\text{Th}(\text{OH})(\text{H}_2\text{PO}_4)_3(\text{aq})$
$\text{ThH}_{-3}(\text{H}_3\text{PO}_4)_4(\text{aq})$	$3.86 \pm 0.04$	$\text{Th}(\text{H}_2\text{PO}_4)_4(\text{aq})$
$\text{ThH}_{-7}(\text{H}_3\text{PO}_4)_5^{3-}$	$-3.65 \pm 0.13$	$\text{Th}(\text{OH})_2(\text{H}_2\text{PO}_4)_5^{3-}$ or $\text{Th}(\text{H}_2\text{PO}_4)_3(\text{HPO}_4)_2^{3-}$

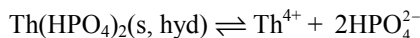
Quantitative solubility experiments have been described in [1956CHU/STE], [1967MOS/ESS], [1994BAG/FOU], [1995OST], [1999FOU/LAG] and [2001THO/DAC]. Moeller *et al.* [1948MOE/SCH] describe the use of phosphate precipitation as an analytical method for the determination of thorium and Matijević and Milić [1963MAT/MIL] describe the use of phosphate to obtain information on colloid precipitation.

Chukhlantsev and Stepanov [1956CHU/STE], measured the solubility of what they claimed were the solid phases  $\text{Th}_3(\text{PO}_4)_4(\text{s})$  and  $\text{Th}(\text{HPO}_4)_2(\text{s})$ ; the composition of the first phase has been questioned [1996BEN/BRA], [1998BRA/DAC], see Section X.2.3.1. The solubilities were measured as a function of pH in nitric and sulphuric acid solutions in the pH range 1.80–2.45; Chukhlantsev and Stepanov noticed a difference in solubility between the two media but made no attempt to analyse the data in terms of a chemical model. They report a solubility product  $\log_{10} K_{s,0} = -(79.2 \pm 0.8)$  in nitric acid and  $\log_{10} K_{s,0} = -(78 \pm 1)$  in sulphuric acid for the reaction:



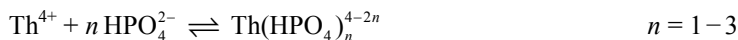
Chukhlantsev and Stepanov found  $\log_{10} K_{s,0} = -57.6$  for  $^{234}\text{Th}$ -doped  $\text{Th}_3(\text{PO}_4)_4(\text{s})$  and suggest that the difference between this value and the other two determinations is due to the formation of  $\text{Th}_3(\text{OH})_3(\text{PO}_4)_3(\text{s})$  but no evidence for this is presented. For reasons given in Appendix A these values have not been accepted by the present review. It can be noted that these values differ significantly from that proposed in [1994BAG/FOU],  $\log_{10} K_{s,0}^\circ = -(112 \pm 2.1)$ .

The equilibrium constant reported by [1956CHU/STE] for the reaction:



was  $\log_{10} K_{s,0} = -(26.6 \pm 0.2)$  in nitric acid and  $\log_{10} K_{s,0} = -(20.9 \pm 0.4)$  in sulphuric acid. When the experiments were repeated using a Th-tracer marked solid, a solubility product of  $\log_{10} K_{s,0} = -19.9$ , with an unknown uncertainty, was obtained; it is not clear from the paper if these experiments have been made in nitric or sulphuric acid. These values are not accepted by this review. Moskvin *et al.* [1967MOS/ESS] have also determined the solubility product for  $\text{Th}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ , but have taken the formation of phosphate complexes into account; their reported solubility product is  $\log_{10} K_{s,0} = -26.89$ .

Moskvin *et al.* [1967MOS/ESS] have reported equilibrium constants,  $\log_{10} \beta_n$ , for the reactions:



from solubility measurements using  $\text{Th}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ . The experiments were made in 0.35 M  $\text{HClO}_4$  by varying the phosphoric acid concentration from 0.1 mM to 1.5 M, but under these conditions it is not possible to determine the proton content of the complexes formed. The equilibrium constants  $\log_{10} \beta_1 = 10.6$ ,  $\log_{10} \beta_2 = 22.6$  and  $\log_{10} \beta_3 = 31.3$ , reported by Moskvin *et al.*, are conditional constants for species that contain 1, 2 and 3 coordinated phosphate groups, but where the proton stoichiometry is unknown. At the high acidity used in [1967MOS/ESS], one expects the formation of complexes containing  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  as ligands as shown in [1951ZEB/ALT]. As these species have not been considered by Moskvin *et al.*, their chemical model is not correct, and the proposed equilibrium constants have not been accepted by this review. The solubility product for  $\text{Th}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ ,  $\log_{10} K_{s,0} = -26.89$ , is considerably smaller than the value  $\log_{10} K_{s,0} = -21$  ( $-19.9$  for the experiments using a  $^{234}\text{Th}$  tracer) proposed in [1956CHU/STE]. In view of the shortcomings indicated above this review has not selected any of the equilibrium constants proposed by Moskvin *et al.*

Baglan *et al.* [1994BAG/FOU] determined the solubility of  $\text{Th}_3(\text{PO}_4)_4(\text{s})$  in 0.01–1 M perchloric acid (the ionic strength was not constant) at room temperature. They calculated  $[\text{Th}^{4+}]$  from the measured total concentration by using the known hydrolysis constants; the concentration of phosphate is so low that phosphate complexes can be neglected. The solubility product at zero ionic strength was calculated using estimates of the activity coefficients of the participating ions, but the procedure is not detailed in the paper. Baglan *et al.* report:

$$\log_{10} K_{s,0}^\circ = -(112.0 \pm 2.1)$$

for the reaction:  $\text{Th}_3(\text{PO}_4)_4(\text{s}) \rightleftharpoons 3\text{Th}^{4+} + 4\text{PO}_4^{3-}$

This value, assumed to apply to 298.15 K, has therefore not been selected by this review, but may be used for scoping calculations.

Fourest *et al.* [1999FOU/LAG] have prepared and carefully characterised the solid  $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7(\text{s})$  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  $\text{NaClO}_4$ . The analysis of the experimental data is in the view of this review ambiguous (Appendix A) and the information provided does not allow selection of equilibrium constants.

In two more recent studies [2006DAC/CLA] and [2006CLA/FOU], the Orsay group has studied the rate of dissolution of  $\beta\text{-Th}_{4-x}\text{U}_x(\text{PO}_4)_4(\text{P}_2\text{O}_7)$  but there are no thermodynamic data in these studies.

Östhols [1995OST] studied the solubility of microcrystalline  $\text{ThO}_2(\text{cr})$  in the pH range 5–13 in the presence of 0.01 and 0.1 M phosphate. He noticed that the solubility  $s = 10^{-6.4}$  M, in the pH range 5–10, 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 10.5–13. There is no information on equilibrium constants for phosphate complexes in this study, but it may be noted that the phosphate complexes are so weak that the hydroxide complexes are dominant 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.

Thomas *et al.* [2001THO/DAC] studied the rate of dissolution of solid solutions of U(IV) and Th(IV) phosphate phases. The paper proposes a reaction mechanism and also gives extensive information on phase characterisation. Of particular interest is the solid  $\text{Th}_2(\text{PO}_4)_2(\text{HPO}_4)\cdot\text{H}_2\text{O}$  for which the authors report a solubility product at zero ionic strength,  $\log_{10} K_{s,0}^\circ = -(66.6 \pm 1.2)$  with a reference to a forthcoming publication; as this is not available to the present review, this solubility product is not accepted.

Zebroski *et al.* [1951ZEB/ALT] have made the most extensive study of the complex formation in the Th(IV)-phosphate system and the only one that can be used to determine the stoichiometry of the complexes formed. The experiments have been made at trace levels of Th(IV) using liquid-liquid extraction at 25°C and an ionic strength of 2.00 M  $(\text{Na,H})\text{ClO}_4$ . The authors report equilibrium constants for the reactions:



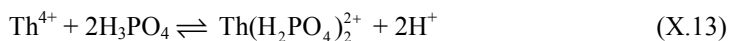
$$\log_{10} \beta (\text{X.10}) = 1.89$$



$$\log_{10} {}^*\beta (\text{X.11}) = 2.18$$



$$\log_{10} {}^*\beta (\text{X.12}) = 4.15$$



$$\log_{10} {}^*\beta (\text{X.13}) = 3.90.$$

There are no uncertainty estimates in [1951ZEB/ALT]. This review has no access to the primary experimental data, but finds no reason to question the quality of this study and has accordingly selected the equilibrium constants proposed by Zebroski *et al.* The stabilities of other actinide(IV) phosphates of similar composition are not known, except for the formation of the corresponding  $\text{Pu}(\text{H}_3\text{PO}_4)^{4+}$  complex,  $\log_{10} \beta^\circ$  (X.10) has a similar value of  $(2.4 \pm 0.3)$  [2003GUI/FAN]. We note also that the stoichiometries of the selected complexes are the same as those for the uranyl(VI)-phosphate system and there is a reasonable linear correlation between the  $\log_{10} \beta^\circ$  values (the equilibrium constants for the reactions  $\text{M} + (n)\text{L} \rightleftharpoons \text{ML}(n)$ , not the reported  $\log_{10} {}^*\beta^\circ$  values) for  $\text{M} = \text{UO}_2^{2+}$  and  $\text{M} = \text{Th}^{4+}$ .

The experimental data of Elyahyaoui *et al.* [1990ELY/BRI] are precise, *cf.* Table X-3, but for reasons given above and in Appendix A the proposed equilibrium constants have not been selected by this review.

From the data of Zebroski *et al.* [1951ZEB/ALT] and assuming the following ion interaction coefficients  $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = \varepsilon(\text{Th}(\text{H}_3\text{PO}_4)^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ ;  $\varepsilon(\text{Th}(\text{H}_2\text{PO}_4)^{3+}, \text{ClO}_4^-) = \varepsilon(\text{Th}(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^{3+}, \text{ClO}_4^-) = \varepsilon(\text{M}^{3+}, \text{ClO}_4^-) \cong (0.5 \pm 0.1) \text{ kg}\cdot\text{mol}^{-1}$ ;  $\varepsilon(\text{Th}(\text{H}_2\text{PO}_4)_2^{2+}, \text{ClO}_4^-) = \varepsilon(\text{M}^{2+}, \text{ClO}_4^-) \cong (0.4 \pm 0.1) \text{ kg}\cdot\text{mol}^{-1}$ , and  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ , we find the following equilibrium constants and Gibbs energies of reaction at 25°C and zero ionic strength:

$$\log_{10} \beta^\circ (\text{X.10}) = (1.89 \pm 0.31) \quad \Delta_r G_m^\circ = -(10.79 \pm 1.77) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10} {}^*\beta^\circ (\text{X.11}) = (3.45 \pm 0.32) \quad \Delta_r G_m^\circ = -(19.69 \pm 1.83) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10} {}^*\beta^\circ (\text{X.12}) = (5.42 \pm 0.32) \quad \Delta_r G_m^\circ = -(30.94 \pm 1.83) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10} {}^*\beta^\circ (\text{X.13}) = (6.20 \pm 0.32) \quad \Delta_r G_m^\circ = -(35.39 \pm 1.83) \text{ kJ}\cdot\text{mol}^{-1}$$

The corresponding standard molar Gibbs energies of formation, calculated using these constants and  $\Delta_f G_m^\circ(\text{Th}^{4+}, 298.15 \text{ K}) = -(704.8 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$  selected by this review are:

$$\Delta_f G_m^\circ(\text{Th}(\text{H}_3\text{PO}_4)^{4+}, 298.15 \text{ K}) = -(1864.9 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th}(\text{H}_2\text{PO}_4)^{3+}, 298.15 \text{ K}) = -(1873.8 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th}(\text{H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^{3+}, 298.15 \text{ K}) = -(3034.5 \pm 6.4) \text{ kJ}\cdot\text{mol}^{-1}$$

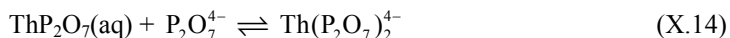
$$\Delta_f G_m^\circ(\text{Th}(\text{H}_2\text{PO}_4)_2^{2+}, 298.15 \text{ K}) = -(3038.9 \pm 6.4) \text{ kJ}\cdot\text{mol}^{-1}$$

There is no information on the enthalpy and entropy of reaction in the Th(IV)-phosphate system.

### X.2.3.3 Other aqueous thorium phosphate species

Filinov *et al.* [1960FIL/TEK] studied the solubility of  $\text{ThP}_2\text{O}_7(\text{s})$  in 0.0237–0.204 M  $\text{Na}_4\text{P}_2\text{O}_7$  solutions and found that the solubility decreased from 0.0205 to 0.0077 M. The paper contains no information of the pH and no thermodynamic data can therefore be

deduced. In solutions of sulphuric, nitric and hydrochloric acid the solubility of  $\text{ThP}_2\text{O}_7(\text{s})$  increased linearly with  $[\text{H}^+]$  but the experimental data are only given in figures and can therefore not be analysed by the present review. The authors suggest an equilibrium constant of  $\log_{10} K (\text{X.14}) = (5.25 \pm 0.17)$  for the stepwise reaction:



There is no justification in [1960FIL/TEK] for the stoichiometry and the equilibrium constant is therefore not accepted by this review. The only conclusion to be drawn from this study is qualitative, that complexes are formed in the Th(IV)-pyrophosphate system.

Merkusheva *et al.* [1967MER/SKO] determined the solubility of  $\text{ThP}_2\text{O}_7(\text{s})$  at  $25^\circ\text{C}$  in a 0.1 M (Na, H) $\text{ClO}_4$  ionic medium by varying the concentration of  $\text{H}^+$  in the various test solutions between 100 and 5 mM and measuring the corresponding concentrations. They report the following equilibrium constants:  $\log_{10} K_{s,0} (\text{X.15}) = -(24.25 \pm 0.02)$  and  $\log_{10} \beta_1 (\text{X.16}) = (18.0 \pm 0.2)$  for the reactions



and



where the uncertainties are those given by the authors; however, the details of the procedure used to deduce them is not clear. 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  $\text{ThH}_p(\text{P}_2\text{O}_7)_q$  (charge omitted for simplicity). The stepwise equilibrium constant for Reaction (X.14),  $\log_{10} K = 5.25$ , seems unexpectedly small compared to the equilibrium constant for Reaction (X.16),  $\log_{10} K = 18.0$ ; for these reasons this review has not accepted the proposed equilibrium constants.

Dissolution of  $\text{Th}_2(\text{PO}_4)(\text{P}_2\text{O}_7)$  and solid solutions of  $(\text{Th,Pu})_2(\text{PO}_4)(\text{P}_2\text{O}_7)$  have been studied by [2002ROB/DAC], but no information on thermodynamic data is given. The dissolution of monazite in carbonate media is discussed in [2002ABD], but here also there is no thermodynamic information.

### X.3 Solid thorium arsenides

The phase diagram of the Th-As system is still quite poorly defined, except for the Th-rich region, which was studied in detail by Benz [1968BEN]. There are three compounds, whose compositions and structures are given in Table X-4. The diarsenide has two forms, with a transformation temperature of *ca.* 1373 K [1966HUL2].

The only studies of thermodynamic data for thorium arsenides are the measurements of the heat capacities of  $\text{ThAs}(\text{cr})$  and  $\text{Th}_3\text{As}_4(\text{cr})$  from 5 to 300 K by

[1980BLA/TRO] and [1980BLA/LAG], see Appendix A. The derived values of the entropy and heat capacity are the selected values:

$$S_m^\circ(\text{ThAs}, \text{cr}, 298.15 \text{ K}) = (79.8 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^\circ(\text{ThAs}, \text{cr}, 298.15 \text{ K}) = (50.5 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{Th}_3\text{As}_4, \text{cr}, 298.15 \text{ K}) = (274.6 \pm 1.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^\circ(\text{Th}_3\text{As}_4, \text{cr}, 298.15 \text{ K}) = (183.3 \pm 1.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

where the uncertainties are estimated by the review.

Table X-4: Structural data for thorium arsenides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)	Reference
ThAs	fcc, $Fm\bar{3}m$	NaCl	$a = 5.972$	[1955FER]
			$a = 5.976 \pm 0.001$	[1968BEN]
			$a = 5.976 \pm 0.001$	[1980BLA/TRO]
Th <sub>3</sub> As <sub>4</sub>	bcc, $I\bar{4}3d$	Th <sub>3</sub> P <sub>4</sub>	$a = 8.843$	[1955FER]
			$a = 8.945 \pm 0.005^*$	[1980BLA/LAG]
$\alpha$ -ThAs <sub>2</sub> < ca. 1473 K	orthorhombic $Pnma$	PbCl <sub>2</sub>	$a = 7.287 \pm 0.003$	[1966HUL2]
			$b = 4.002 \pm 0.002$	
			$c = 9.784 \pm 0.004$	
$\beta$ -ThAs <sub>2</sub> > ca. 1473 K	tetragonal $P4/nmm$	Cu <sub>2</sub> Sb	$a = 4.086$	[1955FER]
			$c = 8.575$	

\* No clear explanation can be given for the large difference between this value and that from [1955FER], unless there is a printing error. A value of  $(8.845 \pm 0.005) \text{ \AA}$  would bring the lattice parameter from [1980BLA/LAG] in more reasonable agreement with the value given by [1955FER] and with their own value for the lattice parameter of U<sub>3</sub>As<sub>4</sub>(cr),  $(8.528 \pm 0.005) \text{ \AA}$ .

## X.4 Solid thorium antimonides

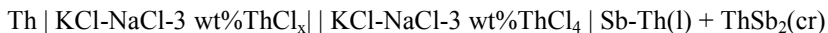
The phase diagram of the Th-Sb system has not been studied systematically. According to Ferro [1956FER], who carried out an X-ray investigation of phases prepared by from the elements at ca. 1273 K, there are three compounds, whose compositions and structures are given in Table X-5.

Table X-5: Structural data for thorium antimonides.

Phase	Symmetry, space group	Structural type	Lattice parameters (Å)	Reference
ThSb	fcc, $Fm\bar{3}m$	NaCl	$a = 6.318$	[1956FER]
Th <sub>3</sub> Sb <sub>4</sub>	bcc, $I\bar{4}3d$	Th <sub>3</sub> P <sub>4</sub>	$a = 9.372$	[1956FER]
ThSb <sub>2</sub>	Tetragonal, $P4/nmm$	Cu <sub>2</sub> Sb	$a = 4.353$	[1956FER]
			$c = 9.172$	



The only thermodynamic data for this system are those reported by Kadochnikov *et al.* [1974KAD/POY], who measured the emf of the cell:



from 939 to 1093 K. From these data, the thorium potential in the diphasic region {Sb(l) + ThSb<sub>2</sub>(cr)} is given by

$$\Delta_f G_m(\text{Th}) = -319173 + 77.574 T \text{ (J}\cdot\text{mol}^{-1}\text{)}.$$

These data cannot be processed further without an assumption regarding the activity of antimony in the saturated Th-Sb liquid. With the very small solubilities of Th in Sb(l), also measured by [1974KAD/POY],  $\log_{10} x_{\text{Th}} = -6820/T + 4.07$ , (giving  $x_{\text{Th}} = 0.0074$  at 1100 K) the activity of Sb will be very little different from the ideal value, and hence the Gibbs energy of formation of ThSb<sub>2</sub>(cr) can be calculated to be:

$$[\Delta_f G_m^\circ]_{939\text{K}}^{1093\text{K}}(\text{ThSb}_2, \text{cr}, T) = -3183400 + 76.76 T \text{ (J}\cdot\text{mol}^{-1}\text{)},$$

where the standard state for Sb is Sb(l), and these values are selected.

## X.5 Solid thorium bismuthides

### X.5.1 Phase diagram and structures

The phase diagram of the Th-Bi system is still rather ill-defined. The most recent study by [1982BOR/BOR2] (who give a tentative phase diagram) indicates the existence of four compounds, whose compositions and structures are given in Table X-6. However, these authors note that the ThBi(cr) may be metastable, and that the Th<sub>5</sub>Bi<sub>3</sub>(cr) phase may be stabilised by minor impurities, like some other phases with this structure. Dahlke *et al.* [1969DAH/GAN] reported the possible existence of a phase more thorium-rich than Th<sub>5</sub>Bi<sub>3</sub>(cr), but this has not been confirmed by subsequent workers –see also Appendix A for further comments on the study by [1969DAH/GAN]. The solubility of thorium in Bi(l) was assessed by [1981CHI/AKH] from six separate studies up to 1974 to be given by the expression:

$$\log_{10} x_{\text{Th}} = -3618/T + 1.513 \quad (688 - 1373 \text{ K})$$

where  $x_{\text{Th}}$  is the mole fraction of thorium in the melt.

Table X-6: Structural data for thorium bismuthides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)	Reference
Th <sub>5</sub> Bi <sub>3</sub>	hexagonal, $P6_3/mcm$	Mn <sub>5</sub> Si <sub>3</sub>	$a = 9.590$ $c = 6.623$	[1982BOR/BOR2]
ThBi	bcc, $Pm\bar{3}m$	CsCl	$a = 3.909$	[1982BOR/BOR2]
Th <sub>3</sub> Bi <sub>4</sub>	bcc, $I\bar{4}3d$	Th <sub>3</sub> P <sub>4</sub>	$a = 9.559$ $a = 9.562$	[1975FER], [1982BOR/BOR2]
ThBi <sub>2</sub>	Tetragonal, $P4/nmm$	Cu <sub>2</sub> Sb	$a = 4.492$ $c = 9.298$ $a = 4.495$ $c = 9.308$	[1975FER] [1982BOR/BOR2]

## X.5.2 Thermodynamic data

### X.5.2.1 Enthalpy of formation

Borzzone *et al.* [1982BOR/BOR2] have reported measurements of the enthalpy of formation at *ca.* 300 K of 13 Th-Bi alloys ranging from Th<sub>0.2</sub>Bi<sub>0.8</sub> to Th<sub>0.75</sub>Bi<sub>0.25</sub>. An isoperibol aneroid calorimeter was used to measure the reaction enthalpy by direct combination of the elements. Reaction was incomplete in the measurements of five further alloys. The resulting enthalpies of formation were consistent with the formation of the four compounds given in Table X-7 and the following values for their enthalpies of formation were derived:

$$\Delta_f H_m^\circ(\text{Th}_5\text{Bi}_3, \text{cr}, 298.15 \text{ K}) = -(532.2 \pm 16.7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThBi}, \text{cr}, 298.15 \text{ K}) = -(162.3 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{Th}_3\text{Bi}_4, \text{cr}, 298.15 \text{ K}) = -(597.5 \pm 14.6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThBi}_2, \text{cr}, 298.15 \text{ K}) = -(207.1 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}$$

and these are the selected values. The small difference in the temperature of measurement and 298.15 K has been ignored.

The general trend of the enthalpies of formation of these compounds appears similar to that observed for compounds of uranium [1968KUB] and a number of lanthanides [1980BOR/BOR] with arsenic, antimony, and bismuth; more generally, these trends are also in satisfactory agreement with those deduced from the model of Miedema *et al.* [1977MIE/BOE].

### X.5.2.2 Gibbs energies

There are three sets of measurements of the thorium–bismuth system: two relatively consistent emf studies around 1000 K, and a Knudsen study which is more difficult to interpret. Wiswall and Egan [1963WIS/EGA] have reported thorium activities in unsaturated solutions in bismuth, measured in an emf cell involving ThCl<sub>4</sub> dissolved in

LiCl-KCl eutectic. They found that at 1073 K the excess Gibbs energy of solution of thorium was constant from  $x_{\text{Th}} = 0.00135$  to 0.0080, and hence for the dissolution  $\alpha\text{-Th} = [\text{Th}]_{\text{Bi}}$ ,  $\Delta_{\text{sln}} G_{\text{m}}(\text{Th}, 1073 \text{ K}) = -118000 + 20542 \cdot \log_{10} x_{\text{Th}}$  ( $\text{J} \cdot \text{mol}^{-1}$ ), with an uncertainty estimated by this review to be  $\pm 3000 \text{ J} \cdot \text{mol}^{-1}$ . Poyarkov *et al.* [1974POY/LEB] made similar measurements (but using NaCl-KCl(l) as the solvent) in the two-phase region {liquid bismuth + compound} from 953 to 1093 K. They suggested that the phase in equilibrium with Bi(l) was  $\text{Th}_3\text{Bi}_4(\text{cr})$ , but the more recent work by [1982BOR/BOR2] indicates that  $\text{ThBi}_2(\text{cr})$  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) +  $\text{ThBi}_2(\text{cr})$ } phase field:  $\Delta_{\text{sln}} G_{\text{m}}(\text{Th}) = -224220 + 67.78 T$  ( $\text{J} \cdot \text{mol}^{-1}$ ), with an uncertainty estimated by the review to be  $\pm 3500 \text{ J} \cdot \text{mol}^{-1}$ . If it is assumed that the constant excess Gibbs energy of solution of thorium measured by [1963WIS/EGA] at 1073 K can be extrapolated to the phase boundary, calculated to be at  $x_{\text{Th}} = (0.0138 \pm 0.0050)$  from the solubility equation assessed by [1981CHI/AKH] noted above, then  $\Delta_{\text{sln}} G_{\text{m}}(\text{Th}, 1073 \text{ K}) = -(156.2 \pm 4.1) \text{ kJ} \cdot \text{mol}^{-1}$ . This is in reasonable agreement with the value of  $-(151.5 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$  given by the study of [1974POY/LEB]. All the uncertainties in these calculations are estimated by the review. The data of [1974POY/LEB] can be used to calculate the Gibbs energy of formation of  $\text{ThBi}_2(\text{cr})$  around 1000 K. With the low solubility of thorium, the chemical potential of bismuth in the melt will be close to the ideal value and  $\Delta_{\text{f}} G_{\text{m}}(\text{ThBi}_2, \text{cr})$  (from Bi(l)) in the temperature range of the study by [1974POY/LEB] is calculated to be:

$$[\Delta_{\text{f}} G_{\text{m}}^{\circ}]_{1950\text{K}}^{1100\text{K}}(\text{ThBi}_2, \text{cr}, T) = -222900 + 66.3 T \quad \text{J} \cdot \text{mol}^{-1}.$$

After allowing for the enthalpy of fusion of Bi(cr) ( $11.3 \pm 0.4$ )  $\text{kJ} \cdot \text{mol}^{-1}$  [1994LAN] the derived enthalpy of formation in this temperature range is thus consistent with that measured at *ca.* 300 K by [1982BOR/BOR2],  $-(207.1 \pm 6.3) \text{ kJ} \cdot \text{mol}^{-1}$ , discussed above, although the entropy change is numerically quite large (*ca.*  $-(25.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$  from Bi(cr)).

The thermodynamic properties of the Th-Bi system have also been studied by Dahlke *et al.* [1969DAH/GAN]. These authors measured the total effusion pressures of (essentially) Bi(g) +  $\text{Bi}_2(\text{g})$  over a number of phase fields in this system (from 884 to 1759 K, depending on the phase field). The pressures, and the composition of the effusing sample, were inferred from weight losses; X-ray diffraction studies were made on a number of quenched samples. As noted in detail in Appendix A, their pressure measurements are not in accord with other published phase diagrams; in particular, no discontinuity in the pressures was observed at the composition  $\text{Th}_3\text{Bi}_3$ . Moreover, Dahlke *et al.* [1969DAH/GAN] found evidence for the formation of a thorium-rich phase with a composition around  $\text{Th}_3\text{Bi}(\text{cr})$ , but this phase has not been observed in any other studies. They also indicated that the monobismuthide phase has a considerable range of homogeneity, from  $\text{ThBi}_{0.8}$  to  $\text{ThBi}_{1.08}$ , for which there is no independent evidence. There is also a more severe problem in their calculation of the individual Bi(g) and  $\text{Bi}_2(\text{g})$  from the effusion rate, since the equation they used for the dimerisation reaction was not

appropriate at higher temperatures. Their results have thus been completely recalculated from the published raw data, as described in Appendix A. The revised Gibbs energies of solution of bismuth in the various diphasic fields are given in Table X-7.

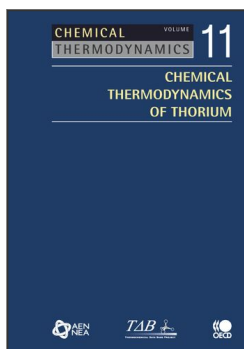
The melt in equilibrium with the most thorium-rich phase contains an unknown amount of bismuth at the temperatures involved (1690–1760 K), so even with corrected bismuth pressures, it is impossible to use these vaporisation data alone to calculate Gibbs energies of formation of the intermediate compounds. However, combination of the bismuth potential in the diphasic field  $\{\text{Th}_3\text{Bi}_4(\text{cr}) + \text{ThBi}_2(\text{cr})\}$  with the Gibbs energy of formation of  $\text{ThBi}_2(\text{cr})$  in a similar temperature range measured by Poyarkov *at al.* [1974POY/LEB], provides an estimate of  $\Delta_f G_m(\text{Th}_3\text{Bi}_4, \text{cr})$  in the temperature range 950–1150 K:

$$[\Delta_f G_m^{\circ}]_{950\text{K}}^{1100\text{K}}(\text{Th}_3\text{Bi}_4, \text{cr}, T) = -605440 + 176.43 T \text{ J}\cdot\text{mol}^{-1}$$

In principle, this could be extended to the remaining phase fields, but owing to uncertain phase boundaries of  $\text{ThBi}(\text{cr})$ , and discrepancies with the phase diagram, this is not thought to be a meaningful proposition.

Table X-7: Bismuth potentials in the diphasic field in the Th-Bi system.

Phase field	$\Delta_{\text{sln}} G_m(\text{Bi}) \text{ (J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\text{)}$	Temperature range (K)
(Th,Bi)(l) + $\text{Th}_3\text{Bi}(\text{cr})$	$-237850 + 29.30 T$	1691–1759
$\text{Th}_3\text{Bi}(\text{cr}) + \text{ThBi}_{1-x}(\text{cr})$	$-147218 + 15.60 T$	1474–1723
$\text{ThBi}_{1+x}(\text{cr}) + \text{Th}_3\text{Bi}_4(\text{cr})$	$-144119 + 54.35 T$	1126–1433
$\text{Th}_3\text{Bi}_4(\text{cr}) + \text{ThBi}_2(\text{cr})$	$-31631 + 11.233 T$	951–1165
$\text{ThBi}_2(\text{cr}) + (\text{Bi,Th})(\text{l})$	$-188 + 0.636 T$	916–1073



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