

## V Thorium elemental

### V.1 Thorium crystal and liquid

#### V.1.1 Crystal structure and phase transitions

Thorium metal has a face centred cubic structure, (space group  $Fm\bar{3}m$ , Cu type) at 298.15 K and undergoes a structural change to a bcc-phase (space group  $Im\bar{3}m$ , W type) at *ca.* 1630 K. The lattice parameters are 5.0842 Å at 298.15 K [1956JAM/STR] and 4.11 Å at 1723 K [1954CHI]. Rand [1975RAN] critically examined the data of 15 studies of this transformation with the reported transition temperatures ranging from 1605 to 1698 K, with most values lying between 1623 and 1653 K. The probable reason for this seemingly wide range of values is the effect of impurities in the thorium used. It is clear that small amounts of carbon, nitrogen and oxygen, which are difficult to remove from thorium, raise the transformation temperature, whereas additions of niobium, tantalum and zirconium tend to lower the temperature of the phase change. We have therefore given considerable weight to the work of Chiotti and Dooley [1967CHI/DOO] ((1623 ± 10) K) and Takeuchi *et al.* [1966TAK/HON] ((1633 ± 10) K) who both extrapolated the transition temperature to zero carbon content and select for the transformation temperature:

$$T_{\text{trs}}(\text{Th, cr}) = (1633 \pm 20) \text{ K.}$$

Glushko *et al.* [1982GLU/GUR] selected the slightly higher, but not inconsistent, value of (1650 ± 20) K, possibly giving more weight to the fact that Levinson [1966LEV] reported two measurements (at 1639 and 1650 K) which apparently referred to the low temperature phase.

The enthalpy of transformation has been taken from the work of Levinson [1966LEV], who investigated the enthalpy of thorium metal to just beyond the melting point and found  $\Delta_{\text{trs}}H_{\text{m}}(\text{Th, cr}) = (3.6 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$ . This value has been confirmed by the more recent study [1996BOI/COL] of some physicochemical properties of thorium (0.5 mass% impurities) up to 5000 K by the very rapid heating technique. No temperatures were measured, but the discontinuity on the electrical resistivity curve at the transition gave a transformation enthalpy of  $3.5 \text{ kJ}\cdot\text{mol}^{-1}$  with an uncertainty estimated by the review to be  $0.2 \text{ kJ}\cdot\text{mol}^{-1}$ .

Rand [1975RAN] and Glushko *et al.* [1982GLU/GUR] also assessed the melting point and enthalpy of fusion of thorium, selecting  $T_{\text{fus}}(\text{Th, } \beta) = (2023 \pm 10) \text{ K}$  from eight studies and  $\Delta_{\text{fus}}H_{\text{m}}(\text{Th, } \beta, 2023 \text{ K}) = (13.8 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$  from Levinson [1966LEV]. As for the enthalpy of transformation, this has been confirmed by the recent work of Boivineau *et al.* [1996BOI/COL]. No other recent studies of the melting point of thorium have been found.

## V.1.2 Heat capacity and entropy

The heat capacity data for Th(cr) are rather unsatisfactory, especially those from 4 to 30 K and a more definitive study with high purity thorium of the values below 300 K is clearly required.

### V.1.2.1 Heat capacity below 298.15 K

The experimental studies in this temperature range are summarised in Table V-1, and shown in Figure V-1 (0 to 300 K) and in more detail for the very low temperature data in Figure V-2 (0 to 35 K).

Table V-1: Experimental studies on  $C_{p,m}$  (Th, cr) below 300 K.

Reference	Temperature range (K)	Comments
[1953GRI/SKO]	18 – 300	No individual points, rounded values from 20 K only. Accuracy estimated by the authors to be 0.1% at 20 K, 0.3% at 30 K and above 35 K, 0.1%
[1955SMI/WOL]	1.2 – 19	Individual points 1.4 – 4 K given on a $C_{p,m}/T$ vs. $T^2$ plot. Above 4 K, the only data given are a (small) plot of $\theta_D$ vs. $T$ (up to 19 K).
[1966GOR/MON]	1.374 – 4	Data from 1 – 2.2 K plotted on a $C_{p,m}/T$ vs. $T^2$ line; further data to 4 K (no details) correspond to a constant $\theta_D = (163.3 \pm 0.7)$ K.
[1972LUE/COT]	1.5 – 5	Deals mainly with the effect of small additions of U to Th, but measurements were made on pure Th. No $C_{p,m}$ values reported, only the values of constant $\gamma$ and $\theta_D = (160.4 \pm 0.5)$ K.
[1973SAT/KUM]	Not given, probably 1 to 4 K	Deals mainly with Th-Y and Th-La alloys, but measurements were made on pure Th. No $C_{p,m}$ values are reported, only plots of $C_{p,m}/T$ vs. $T^2$ , together with the derived constants $\gamma$ ( $4.24 \text{ mJ}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$ ) and $\theta_D$ (166 K). The temperature range of the measurements for pure Th(cr) is not clear. The plotted data for pure Th and Th-Y and Th-rich Th-La alloys extend only to 3.8 K, but to 7.5 K for La-rich Th-La alloys.
[1975SCH/WOL]	Not given, possibly up to 11 K	Data for Th(cr) and $\text{Th}_4\text{H}_{15}$ (cr) were measured. The only values given for Th are $\gamma$ and $\theta_D$ (167 K); the temperature range from which these were derived is not stated. There is a plot of $C_{p,m}/T$ up to 11 K for $\text{Th}_4\text{H}_{15}$ (cr), so it is possible that Th(cr) was studied over the same temperature range.
[1980NAK/TAK]	84 – 991	Values of 213 measurements from 84.15 to 991.32 K are tabulated in detail.

Figure V-1: Heat capacity of Th(cr) from 0 to 300 K.

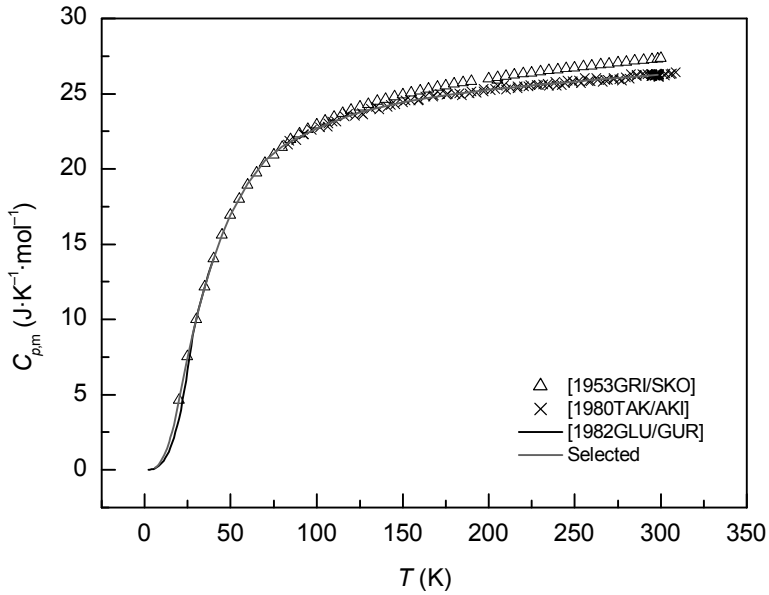
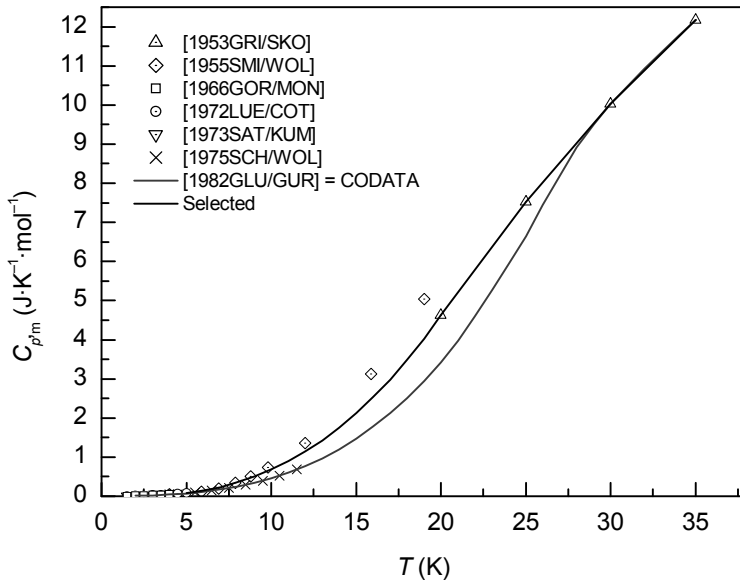


Figure V-2: Heat capacity of Th(cr) from 0 to 35 K.



None of the papers describing the studies below 20 K gives the measured values of  $C_{p,m}$ ; they report only the values of  $\gamma$  and  $\theta_D$  derived from the relation

$$C_{v,m} = \gamma T + (12R/5) \pi^4 (T/\theta_D)^3. \quad (\text{V.1})$$

The difference between  $C_{p,m}$  and  $C_{v,m}$  is quite small ( $< 5 \text{ mJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  up to 35 K), according to the calculations presented in [1953GRI/SKO].

Since the heat capacity values from 4 to at least 20 K are very poorly defined, we shall discuss the relevant publications in some detail. The values of  $\gamma$ , relating to the electronic contribution and  $\theta_D$ , relating to the contribution from lattice vibrations, from these studies are summarised in Table V-2.

Table V-2: Summary of experimental  $\gamma$  and  $\theta_D$  values for Th(cr).

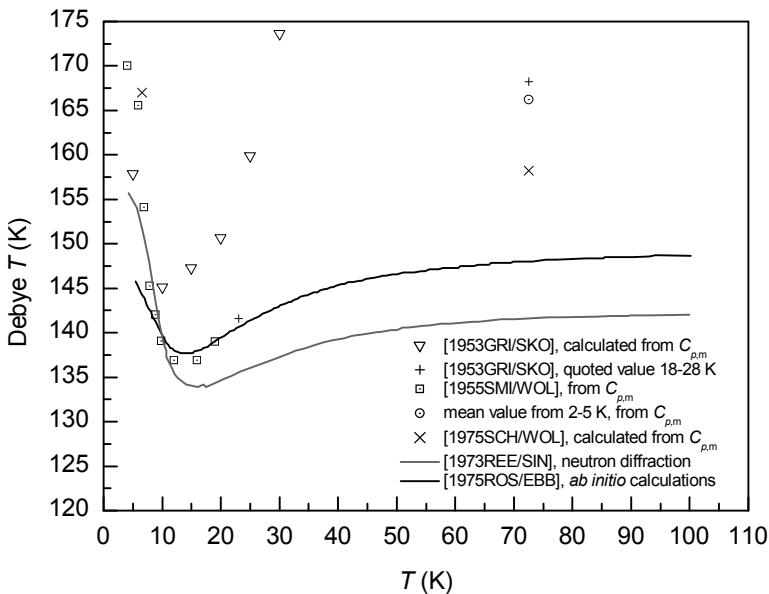
Rerefence	$\gamma$ ( $\text{mJ}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$ )	$\theta_D$ (K)	Temperature range (K)
[1955SMI/WOL]	4.69	Varies with $T$ 0–4 K = 170 10 K = 139 16 K = 137 19 K = 139 (Values above 4 K digitised from a small plot)	1.4–19
[1966GOR/MON]	$4.31 \pm 0.05$	$163.3 \pm 0.7$	1.4–4
[1972LUE/COT]	$4.08 \pm 0.03$	$160.4 \pm 0.5$	1.5–5
[1973SAT/KUM]	4.24	166	1.4–3.8, possibly to 7.5
[1975SCH/WOL]	4.23	167	Not stated, possibly 2–11

However, the temperature range of the measurements from which these values of  $\gamma$  and  $\theta_D$  are derived is also rarely stated explicitly, or even at all. This is important, since although the value of  $\theta_D$  below 4 K is *ca.* 165 K (see Table V-2), the measurements of Smith and Wolcott [1955SMI/WOL], although made on a material containing 200 ppm iron and 50 ppm silicon, indicate clearly that  $\theta_D$  decreases to a minimum of *ca.* 137 K at *ca.* 16 K. This minimum in  $\theta_D$  is the normal behaviour of most metals, including alpha-uranium, as shown in the detailed study of Flotow and Osborne [1966FLO/OSB]. Note that on Figure V-2, values of [1975SCH/WOL] are plotted to 11 K, though these authors do not state the temperature range of their measurements (see Table V-1) (and according to [1955SMI/WOL],  $\theta_D$  is not constant in the range 4–11 K).

There are also two papers which report values of  $\theta_D$  from other sources. Reese *et al.* [1973REE/SIN] describe a neutron diffraction study (at room temperature) to give the phonon distribution (distribution of vibration frequencies), from which the variation of  $\theta_D$  as a function of temperature is derived, and Rosengren *et al.* [1975ROS/EBB]

report a theoretical *ab initio* calculation of  $\theta_D(T)$ . As shown in Figure V-3, from 10 to 20 K, they agree reasonably with each other and rather well with the experimental values from the  $C_{p,m}$  measurements of [1955SMI/WOL]. Above 20 K, they both give  $\theta_D$  values which are much smaller than those derived from the  $C_{p,m}$  measurements of [1953GRI/SKO], and would thus correspond to much bigger heat capacities than the experimental values of [1953GRI/SKO], which seems very unlikely.

Figure V-3: Debye temperature of Th(cr).



Thus, although the best values of  $\theta_D$  above 4 K are not clear, it does seem certain that the Debye temperature has a minimum just below 20 K, and that the use of a constant Debye temperature, particularly that derived from  $C_{p,m}$  measurements in the range 2–10 K is not appropriate.

For temperatures from 20 to 300 K, there are two sets of heat capacity measurements. Griffel and Skochdopole [1953GRI/SKO] reported measurements from 18 to 300 K obtaining a value of  $C_{p,m}^o(298.15\text{ K}) = (27.32 \pm 0.29) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . No anomalies in the low-temperature heat capacity were found, although there was a slight irregularity observed in the measurements from 135 to 155 K. Nakamura *et al.* [1980NAK/TAK] measured the heat capacity of thorium containing 0.05 mass% impurities from 84 to 991 K, using a laser-flash technique. Their measurements agree

with those of [1953GRI/SKO] from 80 to 100 K, but become increasingly lower from 100 to 300 K, with  $C_{p,m}^{\circ}(298.15\text{ K}) = (26.24 \pm 0.13)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

From these rather unsatisfactory experimental data, Glushko *et al.* [1982GLU/GUR] and Ward *et al.* [1986WAR/KLE] have made assessments of the thermal functions. The CODATA assessment [1989COX/WAG] is the same as that by [1982GLU/GUR]. Arblaster [2004ARB] has also provided the reviewers with full details of a thorough assessment (so far unpublished), which gives values very similar to those of [1986WAR/KLE], though made quite independently of it. These reviewers have adopted the same philosophy in selecting the values from 30 to 298.15 K:

- From 30 to 80 K, to accept the values of [1953GRI/SKO] (which are the only data available in this temperature range).
- Above 80 K, to rely heavily on the extensive and well-documented data of Nakamura *et al.* [1980NAK/TAK] from 84 to 991 K, since these merge extremely well with both with the measurements of [1953GRI/SKO] at 80 K and with the high temperature enthalpy data of Levinson [1966LEV] (discussed in Section V.1.2.2) at 1000 to 1200 K.

However, [1982GLU/GUR] and [1986WAR/KLE] extrapolated the heat capacity from 35 K down to 4 K differently, which results in the noticeably different values for  $S(\text{Th, cr, } 298.15\text{ K})$  of  $(51.83 \pm 0.50)$  and  $(52.64 \pm 0.50)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  respectively.

Dr. Bergman at the Glushko Thermocenter, Moscow has kindly provided us with the detailed heat capacity data from 1.374 to 298.15 K selected in [1982GLU/GUR], together with following summary of these selections:

- From 1.37 to 11 K: data from [1975SCH/WOL].
- From 11 to 20 K: extrapolation of data from [1975SCH/WOL], using  $\theta_D = 167\text{ K}$ .
- From 20 to 30 K: smoothed data to reflect the sharp growth of  $C_{p,m}$  from the value extrapolated from the data of [1975SCH/WOL] at 20 K to the experimental value of  $C_{p,m}$  (30 K) from [1953GRI/SKO].
- From 30 to 80 K: data from [1953GRI/SKO].
- From 80 to 298.15 K: data from [1980NAK/TAK].

However, the values of  $\gamma = 4.23\text{ mJ}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$  and a constant  $\theta_D$  of 167 K, used by [1982GLU/GUR] to calculate the  $C_{p,m}^{\circ}$  data from 11 to 20 K, are those obtained by [1975SCH/WOL] from measurements over an unspecified temperature range from 2 K upwards. For reasons stated above, we suggest that this underestimates the heat capacity in this range, (and thus up to 25 K), since  $\theta_D$  is almost certainly smaller than 167 K in this temperature range.

[1986WAR/KLE] accepted the data of [1953GRI/SKO] from 80 down to 20 K; they do not state how they extrapolated the heat capacity to 0 K, but since their value of  $S(\text{Th, cr})$  at 50 K is identical with that given by [1953GRI/SKO], we assume they adopted the values calculated by the latter authors, which as already noted, were derived from the extrapolation to 0 K using a constant  $\theta_D$  of 141.6 K from 0 to 20 K. This is confirmed by the value at 10 K tabulated by [1986WAR/KLE].

In view of the uncertainties in the Debye temperature of Th(cr) discussed in detail above, we have preferred to estimate the  $C_{p,m}$  data from 4 to 20 K without recourse to these uncertain values and have adopted the values suggested to us by Arblaster [2004ARB], who kindly provided us with his recent (so far unpublished) assessment of the thermodynamic properties of Th(cr). For this the selected values are the following:

- From 0 to 4 K: data from [1966GOR/MON], as being representative of the consistent data in this region, including the superconducting transition at 1.374 K.
- From 4 to 20 K: data fitted to a cubic equation in  $T$ , so that  $C_{p,m}$  and  $dC_{p,m}/dT$  are continuous with the values from [1966GOR/MON] at 4 K and from [1953GRI/SKO] at 20 K.
- From 20 to 80 K: data of [1953GRI/SKO].
- From 80 to 300 K: data of [1980NAK/TAK].

These data give  $S_m(\text{Th, cr}, 298.15 \text{ K}) = (52.64 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , where the estimated uncertainty is due principally to the uncertain values of  $C_{p,m}$  from 4 to 20 K (including the effect of the non metallic impurities in the thorium used by [1953GRI/SKO]). Although this value of  $S_m(\text{Th, cr}, 298.15 \text{ K})$  is identical to that given by [1986WAR/KLE], it is calculated entirely independently, with a different procedure for the extrapolation from 20 K down to 0 K (although the data selection from 20 to 300 K is essentially the same).

As a matter of interest, the  $\theta_D$  values calculated from the selected data from 4 to 20 K pass through a minimum of 145.1 K at 10 K and are close to those derived from the  $C_{p,m}$  measurements of [1955SMI/WOL], which perhaps gives added confidence to the selection.

The selected values at 298.15 K are

$$S_m^\circ(\text{Th}, \alpha, 298.15 \text{ K}) = (52.64 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^\circ(\text{Th}, \alpha, 298.15 \text{ K}) = (26.23 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

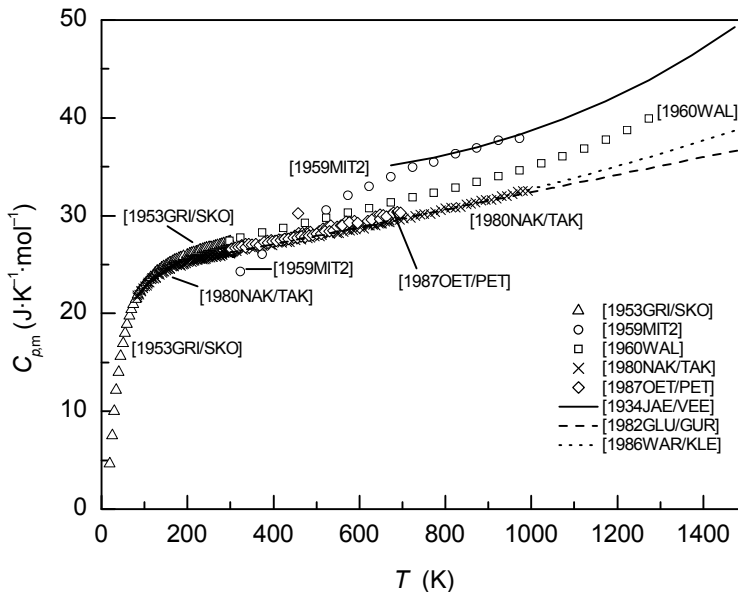
### V.1.2.2 Heat capacity above 298.15 K

There are also inconsistencies in the four measurements of the heat capacity of Th(cr) above 298.15 K (see Table V-3 and Figure V-4).

Table V-3: Experimental studies on  $C_{p,m}$  (Th, cr) above 300 K.

Reference	Temperature range (K)	Comments
[1959MIT2]	323 – 973	Precise details of experimental method not clear, and the data have an unusually high temperature coefficient. These data were not utilised
[1960WAL]	300 – 1273	Data probably too high, and not utilised – see Appendix A
[1980NAK/TAK]	84 – 991	$C_{p,m}$ values of 213 measurements from 84.15 to 991.32 K are tabulated in detail.
[1987OET/PET]	303 – 695	Data agree reasonably well with those of [1980NAK/TAK]

Figure V-4: Heat capacity of Th(cr).



The heat capacity measurements of Wallace [1960WAL] from 298.15 to 1273 K merge smoothly with the low temperature data of [1953GRI/SKO]. However, Nakamura *et al.* [1980NAK/TAK] measured the heat capacity of thorium containing 0.05 mass% impurities using a laser-flash technique. This a valuable study, as not only



are the results given in detail, but the 206 measurements extend from 84 to 991 K using the same equipment, thus obviating the awkward join normally required between low temperature adiabatic calorimetry and other techniques used at higher temperatures. Their measurements agree with those of [1953GRI/SKO] from 80 to 100 K, but become increasingly lower from 100 to 300 K, with  $C_{p,m}^{\circ}$  (298.15 K) = 26.24 J·K<sup>-1</sup>·mol<sup>-1</sup>. Later adiabatic measurements by [1987OET/PET] from 303 to 695 K are slightly higher than those of [1980NAK/TAK], but appreciably below those of Wallace [1960WAL]. There are also  $C_{p,m}$  measurements by Mit'kina [1959MIT2] which are even higher than those of Wallace above 500 K, with an unusually high temperature coefficient.

The only reliable enthalpy increment measurements are those of Levinson [1966LEV] from 1269 to 2100 K, although Jaeger and Veenstra [1934JAE/VEE] reported measurements on thorium containing 6 mass% ThO<sub>2</sub>, which are clearly too high.

As noted earlier, the assessments of the reviews of [1982GLU/GUR] and [1986WAR/KLE] (and the unpublished assessment of Arblaster) have relied heavily on the extensive and well-documented data of Nakamura *et al.* [1980NAK/TAK] from 80 to 1000 K, since these merge extremely well with the high temperature enthalpy data of Levinson [1966LEV] and we have adopted the same philosophy.

The selected values above 298.15 K are those of [1982GLU/GUR], but with a transformation temperature of (1633 ± 20) K rather than (1650 ± 20) K, as discussed earlier. These values are essentially identical to the assessment of [1986WAR/KLE] up to 1000 K, but above this temperature, the  $C_{p,m}$  equation of [1982GLU/GUR] reproduces the enthalpy data of [1966LEV] better than that of [1986WAR/KLE] and has been preferred.

$$[C_{p,m}^{\circ}]_{298.15\text{K}}^{1633\text{K}}(\text{Th}, \alpha, T) = 23.435 + 8.945 \times 10^{-3} T + 1.14 \times 10^6 T^{-2} \quad \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{trs}} H_m(\text{Th}, \text{cr}, 1633 \text{ K}) = (3.6 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$[C_{p,m}^{\circ}]_{1633\text{K}}^{2023\text{K}}(\text{Th}, \beta, T) = 15.702 + 1.1950 \times 10^{-2} T \quad \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{fus}} H_m(\text{Th}, \text{cr}, 2023 \text{ K}) = (13.8 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$[C_{p,m}^{\circ}]_{2023\text{K}}^{3000\text{K}}(\text{Th}, \text{l}) = 46.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

## V.2 Thorium ideal monoatomic gas

### V.2.1 Heat capacity and entropy

The early calculations of the thermal functions of Th(g) (*e.g.* [1965FEB/HER]) used the 200 or so energy levels published by Zalubas [1959ZAL]. In subsequent calculations, Rand [1975RAN] and Oetting *et al.* [1976OET/RAN] used the 523 levels up to 40000 cm<sup>-1</sup> given in a later paper by Zalubas [1968ZAL]. It is not clear how many levels Glushko *et al.* [1982GLU/GUR] and Ward *et al.* [1986WAR/KLE] used in their calculations, but their calculated values are very similar to those of [1976OET/RAN].

Blaise and Wyart [1992BLA/WYA] have more recently published a comprehensive listing of the known energy levels of all the actinide gases, which contains 693 levels for Th(g), and we have used these in our calculations. The lowest levels of the seven configurations below the ionisation level so far unidentified, estimated by Brewer [1971BRE], have also been added in the current calculation. The Gibbs energy functions differ from those given by [1982GLU/GUR] and [1986WAR/KLE] by less than  $0.01 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at all temperatures up to 3000 K after allowing for the different standard-state pressure. The values at 298.15 K are:

$$C_{p,m}^{\circ}(\text{Th, g, 298.15 K}) = (20.790 \pm 0.005) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ}(\text{Th, g, 298.15 K}) = (190.170 \pm 0.010) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The derived heat capacity equation at low temperatures is:

$$[C_{p,m}^{\circ}]_{298.15\text{K}}^{700\text{K}}(\text{Th, g, } T) = 24.1480 - 1.45623 \times 10^{-2} T + 1.77473 \times 10^{-5} T^2 \\ - 5.27700 \times 10^{-4} T^{-2} \quad \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

## V.2.2 Enthalpy of formation

The early measurements of the vapour pressure of thorium are all vitiated by the problem of oxygen contamination, as discussed by Rand [1975RAN] and Glushko *et al.* [1982GLU/GUR]. Therefore we consider below only the two more recent measurements in which this problem was explicitly considered. The vapour pressure of solid thorium was determined by the Langmuir evaporation method in the temperature range of 1757 to 1956 K by Darnell *et al.* [1960DAR/MCC]. Their sublimation pressure corresponds to  $\log_{10}(p/\text{bar}) = -(28780 \pm 620)/T + (5.997 \pm 0.333)$ . From this equation and the selected thermal functions, the derived enthalpy of sublimation for thorium metal at 298.15 K is  $(581.6 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$  by a third-law analysis and  $(561.5 \pm 23.7) \text{ kJ}\cdot\text{mol}^{-1}$  by a second-law analysis. The study by Ackermann and Rauh [1972ACK/RAU], discussed below, suggests that the measurements of [1960DAR/MCC] were probably significantly too high due to oxygen contamination, and the consequent formation of ThO(g). Although Darnell *et al.* attempted to reduce the oxygen contamination (initially  $\sim 1000$  ppm) of their sample by volatilisation of ThO(g) for 200 h at 1883 K, their sample still contained 30 ppm oxygen. Moreover, their resulting steady-state vapour pressures are greater by a factor of about three than those reported by Ackermann and Rauh [1972ACK/RAU] who measured the vapour pressure of crystal-bar thorium, which normally contains 50–100 ppm oxygen, by the target-effusion method, only after the intensity of ThO<sup>+</sup>(g) had decreased to less than 0.5% of that of Th<sup>+</sup>(g) as observed mass-spectrometrically; initially the ThO<sup>+</sup>(g) intensity was approximately five times that of Th<sup>+</sup>(g). It is, therefore, quite likely that the vapour in pseudo steady-state conditions observed by Darnell *et al.* still contained appreciable amounts of ThO(g). Indeed the calculated pressure of ThO(g) in oxygen-saturated Th is about a factor of 100 greater than that of Th(g) from 2000 to 3000 K.

In their investigation, Ackermann and Rauh [1972ACK/RAU] measured the vapour pressure of liquid thorium containing less than 3 at.% dissolved tungsten from 2010 to 2460 K by combined mass-effusion and mass-spectrometric techniques and derived the vapour pressure equation equivalent to:

$$\log_{10}(p/\text{bar}) = -(29770 \pm 440)/T + (6.030 \pm 0.196)$$

from 2010 to 2460 K.

The third-law  $\Delta_{\text{vap}}H_{\text{m}}$  (298.15 K) from these data is  $(601.8 \pm 4.2)$   $\text{kJ}\cdot\text{mol}^{-1}$ , with only a small trend with temperature and a second-law value  $(597.0 \pm 8.4)$   $\text{kJ}\cdot\text{mol}^{-1}$ . The results of Ackermann and Rauh are selected because of the more complete description of the role of oxygen contamination and the good agreement of the second- and third-law values of  $\Delta_{\text{vap}}H_{\text{m}}$  (298.15 K):

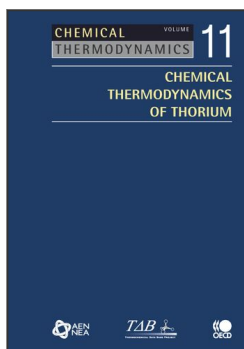
$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th, g, 298.15 K}) = (602 \pm 6) \text{kJ}\cdot\text{mol}^{-1}.$$

This is identical to the value selected by the CODATA Key Values group [1989COX/WAG].

Gingerich [1969GIN2] detected very small amounts of  $\text{Th}_2(\text{g})$  molecules in a mass-spectrometric study of the Th-B-P system and, using the estimated molecular parameters of  $\text{Th}_2(\text{g})$  ( $\omega_{\text{e}} = 92.2 \text{ cm}^{-1}$ ;  $r_{\text{e}} = 3.30 \text{ \AA}$ ; doublet ground state), suggested that  $D^{\circ}(\text{Th}_2, \text{g, 0 K}) \leq (285 \pm 33) \text{ kJ}\cdot\text{mol}^{-1}$  giving  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Th}_2, \text{g, 298.15 K}) > (914 \pm 34) \text{ kJ}\cdot\text{mol}^{-1}$ , and  $S_{\text{m}}^{\circ}(\text{Th}_2, \text{g, 298.15 K}) = 289 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at 298.15 K (values recalculated by the reviewers). This is an unusually high value for the dissociation energy and these values for  $\text{Th}_2(\text{g})$  are given for information only, and are not selected. The calculated fraction of dimer in the saturated vapour is less than 0.1% even at the (extrapolated) boiling point, around 5000 K.

The above selections yield:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{Th, g, 298.15 K}) = (561.0 \pm 6.0) \text{kJ}\cdot\text{mol}^{-1}.$$



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