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Thermochemical and thermophysical properties of curium and its oxides

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Abstract

A consistent set of thermophysical and thermochemical properties of Cm(cr), Cm(g), $Cm^{3+}(aq)$, $Cm^{4+}(aq)$, $Cm^{2+}(aq), Cm_2O_3(cr), CmO_2(cr)$ and CmO(g) is presented. The data have been obtained from critical assessment of experimental determinations published in literature which are supplemented by estimates that are principally based on the extrapolation of trends in the lanthanide series to the actinide series. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Considerable interest in the use of curium (^{244}Cm) as isotopic power sources existed in the US in the 1960s and 1970s. In support of this programme, significant efforts have been made to characterise curium metal and the curium oxides using material produced in kilogram quantities at Savannah River. Most of the data generated have been collected in the Curium Data Sheets prepared at Oak Ridge National Laboratory [1], which are still an important source of information today. Also in the Gmelin Handbook of Inorganic Chemistry, this information is summarised comprehensively [2,3]. However, the results of more recent studies, of which some were made with the less active ^{248}Cm isotope, make it possible to present a more complete set of thermophysical and thermochemical data, to be included in the ITU actinide/lanthanide material property database (*f*-MPD).

Our current interest in the thermophysical and thermochemical properties of curium and its compounds orginates from the studies of novel ways to manage the minor actinides that are present in the radioactive waste from nuclear reactors. Partitioning and transmutation (P&T) as well as partitioning and conditioning (P&C) of minor actinides are being considered as means to minimise the radiological impact of underground storage of radioactive waste. In the case of P&T the actinides are separated from the spent fuel and irradiated in the form of a fuel or a target (metallic or ceramic forms such as oxides and nitrides) to convert them into short-lived elements by fission. In the case of P&C, the separated actinides are incorporated in a durable ceramic waste form that can be stored safely in a repository for a very long time.

In order to understand the behaviour of curium in targets for transmutation or for conditioning, knowledge of the thermochemical and thermophysical properties of curium and its compounds is required. In this paper, data for the curium element states Cm(cr) and Cm(g), curium aqueous ions $Cm^{3+}(aq)$, $Cm^{4+}(aq)$, and $Cm^{2+}(aq)$, and the curium oxides $Cm_2O_3(cr)$, $CmO_2(cr)$ and CmO(g) will be presented.

2. Cm(cr,l)

2.1. Phase transformations and melting point

Curium has a double hexagonal close-packed crystal structure at room temperature, isostructural with α-La (space group $P6_3/mmc$). Like most lanthanide metals, curium undergoes a phase change to a face-centered cubic structure (space group $Fm\bar{3}m$) at high-temperatures [4]. The temperature of the hcp-to-fcc transition is

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not exactly known. It has been suggested [5–7] that the transition is about 50 K below the melting point as is the case for gadolinium, the iso-electronic lanthanide element. This suggestion is adopted here.

Two concordant experimental values for the melting point of curium have been reported, (1613 ± 40) K [8] and (1623 ± 60) K [9], for samples of different purities. As these measurements very likely refer to the IPTS-48 temperature scale, a correction of +1.3 K to the ITS-90 temperature scale is required [10]. The selected melting point is the average of the two corrected values, $T_{\mathrm{fus}} = (1619 \pm 50)$ K.

2.2. Heat capacity and entropy

Heat capacity measurements for curium have not been reported. Ward et al. [6] assumed the free energy function of curium to be identical to that of the lanthanide analogue gadolinium, based on the argument that the actinide curium exhibits lanthanide properties. With these data they analysed their vapour pressure measurements (see below) and found an excellent agreement between the second-law and third-law enthalpy of sublimation, which suggests that the standard entropy is indeed close to that of the iso-electronic lanthanide gadolinium.

This assumption is supported by the comparison of the standard entropies of the actinide and lanthanide metals. In Fig. 1 it can be seen that the entropy of the lanthanide metals, which are all magnetic except for La and Lu, is composed of a lattice component, approximated by the straight line between La and Lu, and an excess component. The actinide metals Ac to Am, on the other hand, are non-magnetic, which is evident from the fact that the experimental entropies of Th–Am are close to the lattice entropies of the lanthanides. The entropy of Cm thus can be approximated by adding S_{exs} for Gd (14.3 J K^{-1} mol^{-1}) to the entropy of Am (55.4 J K^{-1} mol^{-1} [11]), giving $S^{\circ}(298.15\ \mathrm{K}) = 69.7$ kJ mol^{-1}, which is indeed close to the standard entropy of Gd, $S^{\circ}(298.15\ \mathrm{K}) = (68.07 \pm 0.21)$ kJ mol^{-1} [12]. Ward and Hill [13] used a similar approach in which the 'non-magnetic' contribution was estimated from the first two terms in the formula:

$$S^{\circ}_{\mathrm{u}}(298.15\ \mathrm{K}) = S^{\circ}_{\mathrm{k}}(298.15\ \mathrm{K})(r_{\mathrm{u}}/r_{\mathrm{k}}) + \frac{3}{2}R\ln(M_{\mathrm{u}}/M_{\mathrm{k}}) + S_{\mu}, \tag{1}$$

in which the subscript u refers to the unknown element and k to a known element, which for the case of Cm was Gd, Tm and Am. The magnetic contribution at room temperature S_{μ} was calculated from the ground state degeneracy of the Cm atom ($S_{\mu} = R\ln(2J+1) = R\ln(8) = 17.28$ J K^{-1} mol^{-1}). They thus obtained $S^{\circ}(298.15\ \mathrm{K}) = (72.0 \pm 0.8)$ J K^{-1} mol^{-1}. We select the mean of the estimated values, to give

$$S^{\circ}(\mathrm{Cm,\ cr}, 298.15\ \mathrm{K}) = (70.8 \pm 3.0)\ \mathrm{J\ K^{-1}\ mol^{-1}}. \tag{2}$$

Following the suggestion of Ward et al. [6] the heat capacity of curium metal was assumed to be identical to that of gadolinium metal [14].

$$\begin{aligned} &C_{\mathrm{p}}(\alpha\text{-Cm}, T)/\mathrm{J\ K^{-1}\ mol^{-1}} \\ &\quad = 28.409 - 8.284 \times 10^{-4}(T/\mathrm{K}) + 4.920 \times 10^{-6}(T/\mathrm{K})^2, \\ &C_{\mathrm{p}}(\beta\text{-Cm}, T)/\mathrm{J\ K^{-1}\ mol^{-1}} = 28.3, \\ &C_{\mathrm{p}}(\text{liquid-Cm}, T)/\mathrm{J\ K^{-1}\ mol^{-1}} = 37.2. \end{aligned} \tag{3}$$

The enthalpy of fusion is calculated as $\Delta_{\mathrm{fus}}H^{\circ} = 13.86$ kJ mol^{-1} from the difference in the slope of the vapour pressure equations for solid and liquid Cm given by Ward et al. [6]. However, the melting point used by Ward et al. (1640 K) is higher than the one selected here. From the re-fitted equations (see below) a somewhat higher value, $\Delta_{\mathrm{fus}}H^{\circ} = 16.20$ kJ mol^{-1}, is obtained. This value likely includes the enthalpy of transition. Assuming that the ratio between $\Delta_{\mathrm{trs}}H^{\circ}$ and $\Delta_{\mathrm{fus}}H^{\circ}$ for Cm is the same as for Gd, we obtain

$$\begin{aligned} &\Delta_{\mathrm{trs}}H^{\circ}(1568\ \mathrm{K}) = (4.5 \pm 0.5)\ \mathrm{kJ\ mol^{-1}}, \\ &\Delta_{\mathrm{fus}}H^{\circ}(1619\ \mathrm{K}) = (11.7 \pm 1.0)\ \mathrm{kJ\ mol^{-1}}. \end{aligned} \tag{4}$$

2.3. Thermal expansion

Surprisingly, the linear thermal expansion of curium metal has not been measured. The ORNL curium data sheets [1] list the values for americium, $\alpha_{\mathrm{a}} = 7.5 \times 10^{-6}\ \mathrm{K}^{-1}$ and $\alpha_{\mathrm{c}} = 6.2 \times 10^{-6}\ \mathrm{K}^{-1}$ at 293 K, as derived by McWhan et al. [15] from measurements between 153 and 878 K. Fig. 2 shows that this assumption can be justified as the product of melting temperature (T_{m}) times the coefficient of linear thermal expansion at half the melting point ($\alpha_{(T_{\mathrm{m}}/2)}$) of americium falls in the trend the lanthanide series, and not in the trend for the lighter actinide metals. This can be explained by the fact that Am is the first actinide that exhibits lanthanide properties. From this figure we estimate for curium

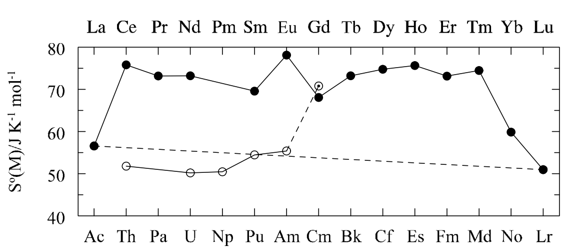

Fig. 1. The variation of the $S^{\circ}(298.15\ \mathrm{K})$ in the actinide (○) and the lanthanide metals (●). The estimated value for Cm(cr) is indicated by ⊙.

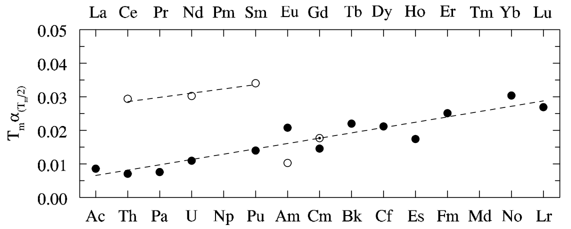

Fig. 2. The variation of the $T_m \cdot \alpha_{(T_m/2)}$ in the actinide (○) and the lanthanide metals (●). The estimated value for Cm(cr) is indicated by ⊙.

$T_m \cdot \alpha_{(T_m/2)} = 0.0177$. Using this value, the linear thermal expansion is approximated by the equation

$$\Delta L/L_0 = -0.3262 + 10.94 \times 10^{-4}(T/\mathrm{K}), \qquad (5)$$

where $\Delta L/L_0$ is the linear thermal expansion (in %). ΔL is zero at 298 K.

2.4. Thermal conductivity

The thermal conductivity of curium metal has not been measured. The curium data sheets [1] give $\lambda(300\ \mathrm{K}) = 10\ \mathrm{W\ m^{-1}\ K^{-1}}$, based on the rough estimates by Ho et al. [16]. This value is close to that of its lanthanide analogue Gd for which $\lambda(300\ \mathrm{K}) = (10.5 \pm 5.0)\ \mathrm{W\ m^{-1}\ K^{-1}}$ has been reported [16]. At 300 K the lattice (λ_{lat}) and electronic (λ_e) components are about equal [17].

The electrical resistivity measurements (5–300 K) of Cm metal reported by Schenkel [18] may help us to make a more reliable estimate. Schenkel obtained $\rho(300\ \mathrm{K}) = 125 \times 10^{-8}\ \Omega\ \mathrm{m}$. The Wiedemann–Franz law, which states that the ratio between thermal conductivity and electric conductivity ($\sigma = 1/\rho$) is about constant for metals [16] ($\lambda/(\sigma T) = 2.44 \times 10^{-8}\ \mathrm{W}\,\Omega\,\mathrm{K^{-2}}$), which then suggests that $\lambda(300\ \mathrm{K}) \simeq 5\ \mathrm{W\ m^{-1}\ K^{-1}}$ for Cm. However, as shown in Fig. 3 this ratio is significantly higher in the mid of the lanthanide series, due to the significant contribution of λ_e. Assuming that $\lambda/(\sigma T)$ for Cm is the same as for Gd, for which $\lambda/(\sigma T) = 4.8 \times 10^{-8}\ \mathrm{W}\ \Omega\ \mathrm{K^{-2}}$ at room temperature, we obtain $\lambda(300\ \mathrm{K}) = 10.0\ \mathrm{W\ m^{-1}\ K^{-1}}$ identical to the value estimated by Ho et al. [16].

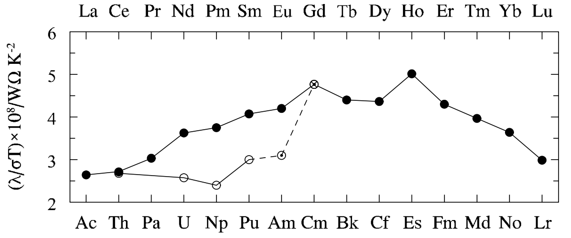

Fig. 3. The variation of the $\lambda/(\sigma T)$ in the actinide (○) and the lanthanide metals (●) at 298.15 K. The estimated values for Cm(cr) and Am(cr) are indicated by ⊙.

At higher temperatures the thermal conductivity can also be estimated from the values for gadolinium metal, which have been been derived by Zinov'ev et al. [17] from thermal diffusivity measurements. These data show an almost linear increase of λ in the temperature range 900–1500 K and Zinov'ev et al. showed that this increase is mainly due to λ_e. As one may expect that λ_e is about equal for Gd and Am, we assume the same dependence for curium, obtaining

$$\lambda/\mathrm{W\ m^{-1}\ K^{-1}} = 7.32 + 8.69 \times 10^{-3}\ (T/\mathrm{K}). \qquad (6)$$

3. Cm(g)

3.1. Heat capacity and entropy

The thermal functions of Cm(g) have been calculated from the electronic energy levels listed by Wordan and Conway [19], Worden et al. [20] and by Brewer [21]. The listing by the latter author is principally based on the assignment by Wordan and Conway but is supplemented by estimations of several unobserved levels. For the standard entropy we obtain

$$S^\circ(\mathrm{Cm,\ g}, 298.15\ \mathrm{K}) = (197.5 \pm 5.0)\ \mathrm{J\ K^{-1}\ mol^{-1}}. \qquad (7)$$

The calculated heat capacity values up to 3000 K have been fitted to the polynomial equations given in Table 1.

3.2. Enthalpy of formation

The vapour pressure of curium has been measured by Smith et al. [5] from 1179 to 2068 K and by Ward et al. [6] from 1327 to 1972 K using a Knudsen effusion technique. The results of the two studies are in fair agreement (Fig. 4), the difference probably being due to the use of a rather impure sample by Smith et al. which contained up to 5 at% ^{240}Pu. The large scatter and the lack of internal consistency in the data by Smith et al. also point towards experimental difficulties. Ward et al. used a high purity sample (triply distilled) and their results are therefore considered to be more precise. They can be represented by the equation

$$\log(p/p^\circ) = 6.167 - 19732(T/\mathrm{K})^{-1} \qquad (8)$$

and for Cm(l) by

$$\log(p/p^\circ) = 5.587 - 18886(T/\mathrm{K})^{-1}, \qquad (9)$$

where p° is the reference pressure (1 atm). From the experimental results we calculate by third-law analysis

Table 1
The heat capacity coefficients of Cm(g); the calculated values have been fitted to the equation $C_p^\circ/\mathrm{J\ K^{-1}\ mol^{-1}} = a(T/\mathrm{K}) + b(T/\mathrm{K})^2 + c(T/\mathrm{K})^3 + d(T/\mathrm{K})^4 + e(T/\mathrm{K})^5 + f$

T/K	$a \times 10^2$	$b \times 10^5$	$c \times 10^9$	$d \times 10^{12}$	$e \times 10^{15}$	f
298.15–1400	8.9428	−19.3085	184.4715	−83.2560	14.5870	14.3455
1400–3000	−3.0383	2.4612	−9.9051	2.1103	−0.18472	40.2607

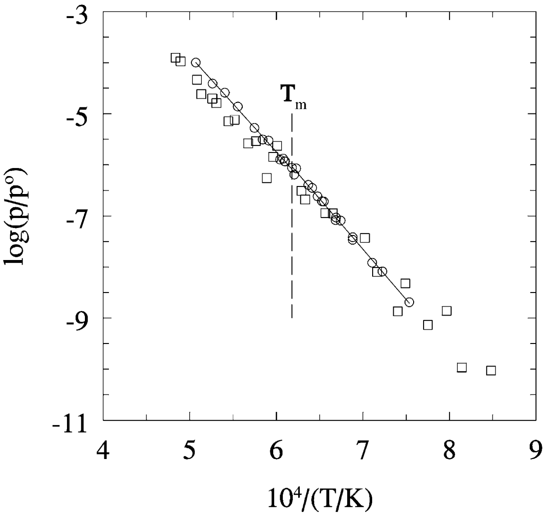

Fig. 4. The vapour pressure of Curium: ○ [6], □ [5].

for the enthalpy of sublimation at 298.15 K, which equals the enthalpy formation, $\Delta_{\mathrm{sub}}H^\circ(298.15\ \mathrm{K}) = (384.2 \pm 0.7)\ \mathrm{kJ\ mol^{-1}}$ from the data for the solid phase (1327–1605 K, the point at 1611 K being excluded after a statistical test) and $\Delta_{\mathrm{sub}}H^\circ(298.15\ \mathrm{K}) = (384.2 \pm 0.9)\ \mathrm{kJ\ mol^{-1}}$ from the data for the liquid phase (1618–1972 K). The corresponding values from the study of Smith et al. are $\Delta_{\mathrm{sub}}H^\circ(298.15\ \mathrm{K}) = (384.3 \pm 4.9)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{\mathrm{sub}}H^\circ(298.15\ \mathrm{K}) = (395.3 \pm 3.6)\ \mathrm{kJ\ mol^{-1}}$, respectively. We select

$$\Delta_f H^\circ(\mathrm{Cm, g}, 298.15\ \mathrm{K}) = (384 \pm 10)\ \mathrm{kJ\ mol^{-1}}, \tag{10}$$

giving most weight to the solid-state data.

4. $\mathrm{Cm^{3+}}$(aq)

4.1. Entropy

The standard molar entropies of the trivalent actinide ions are poorly known. The data for $\mathrm{U^{3+}}$–$\mathrm{Pu^{3+}}$ presented in the NEA-TDP reports [11,22,23] are derived from analyses of experimental studies, though only the value for $\mathrm{Pu^{3+}}$ is based on a calorimetric determination [24]. Estimates for the transplutonium ions are generally based on comparison to the lanthanide series. The variation in the standard entropies of the lanthanide(III) aqueous ions is shown in Fig. 5. This variation can be described with reasonable accuracy by adding the electronic entropy $R\ln(2J+1)$ (neglecting possible ligand field splitting in aqueous solutions) to the entropy value interpolated from the values for La and Lu. If it is assumed that the variation for the actinides(III) ions is parallel to that of the lanthanide(III) ions but shifted as deduced from the experimental values for $\mathrm{Pu^{3+}}$, we obtain for $\mathrm{Cm^{3+}}$ the value $(-207.7 + R\ln(8)) = -190.5\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

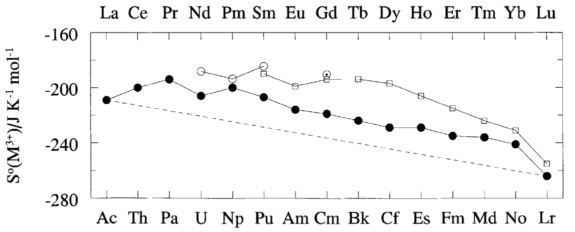

Fig. 5. The variation of S°(298.15 K) for the trivalent lanthanide (●) and actinide (○, □) aqueous ions. The actinide(III) values indicated by ○ are from the NEA-TDP reports [11,22,23] and are based on analyses of experimental studies, those indicated by □ are estimated values from the work of David et al. [27]. The estimated value for Cm(cr) is indicated by ⊙.

Hinchey and Cobble [24] calculated the entropies of the $\mathrm{An^{3+}}$ ions as the sum of the electronic term and a term depending on the radius of the ion. The latter was estimated assuming that the variation of the entropies with ionic radius for the actinide(III) ions is identical to that observed for the lanthanide(III) ions [25]. For $\mathrm{Cm^{3+}}$(aq) they thus obtained $S^\circ(298.15\ \mathrm{K}) = -188.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$. This value was adopted by Fuger and Oetting [26] who assigned an uncertainty of $\pm 12.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

David et al. [27–29] assumed the entropy to be sum of three terms related to the electronic configuration (S_e), the mass (S_M) and the structure of the hydrated aqueous actinide ion (S_h).

$$S(M^{3+}) = S_e + S_M + S_h. \tag{11}$$

S_e was calculated from the ground state degeneracy ($R\ln(2J+1)$) and S_M from the atomic mass ($\frac{3}{2}R\ln M$). S_h was obtained by interpolation of the lanthanide data since the lanthanide and transplutonium ions exhibit the same dependence between hydration and radius. They thus obtained for Cm^{3+}(aq) the value $S°(298.15\ K) = -194\ J\ K^{-1}\ mol^{-1}$.

We select for the standard entropy of Cm^{3+} the mean of these three (not completely independent) estimates, giving

$$S°(Cm^{3+}, aq, 298.15\ K) = -(191 \pm 10)\ J\ K^{-1}\ mol^{-1}. \qquad (12)$$

4.2. Enthalpy of formation

The enthalpy of formation of the Cm^{3+}(aq) ion has been assessed by Fuger and Oetting [26]. They selected $\Delta_f H°(298.15\ K) = -(614.5 \pm 6.6)\ kJ\ mol^{-1}$, solely based on the results of Fuger et al. [30] for the dissolution of ^{244}Cm(cr) in HCl(aq). This measurement was considered more accurate than the earlier measurements by Morss [31] and Wallmann et al. [32,33], also made for ^{244}Cm(cr). Since that time, only a single experimental study has become available. Raschella et al. [34] measured the enthalpies of solution of ^{248}Cm(cr) in 1.0 and 6.0 mol dm^{-3} HCl(aq) using samples that were not intended for calorimetric measurements. They obtained $\Delta_{sln}H°(298.15\ K) = -(606.5 \pm 11.7)\ kJ\ mol^{-1}$ and $-602.4\ kJ\ mol^{-1}$, respectively. The former value is in reasonable agreement with the result of Fuger et al. [30], but as the measurements by Fuger et al. were made with significantly better characterised material, the selected value for the enthalpy of solution of Cm(cr) in 1.0 mol dm^{-3} HCl(aq) is based on this result only: $\Delta_{sln}H°(298.15\ K) = -(614.5 \pm 6.0)\ kJ\ mol^{-1}$ (Table 2). To obtain the enthalpy of formation of Cm^{3+}(aq) this value should be corrected to zero ionic strength. Extrapolation of the data of Raschella et al. [34] yields a correction for the enthalpy of solution of $\Delta H = -0.7\ kJ\ mol^{-1}$. Assuming the difference between 1.0 mol dm^{-3} HCl(aq) and H_2O to be the same as for Am^{3+}, Fuger et al. [35] gives $\Delta H = -0.5\ kJ\ mol^{-1}$. The resulting value for the enthalpy of formation of the Cm^{3+}(aq) ion is

$$\Delta_f H°(Cm^{3+}, aq, 298.15\ K) = -(615.0 \pm 6.0)\ kJ\ mol^{-1}. \qquad (13)$$

From these data one obtains $\Delta_f H°(Cm^{3+}$, aq, $298.15\ K) = -(595.4 \pm 11.0)\ kJ\ mol^{-1}$, which compares well with the value, $-599.2\ kJ\ mol^{-1}$, derived from the standard potential of the Cm^0/Cm^{3+} couple ($E^0 = 2.07$ V) measured by Samhoun and David [36,37] by radiopolarography.

5. Cm^{4+}(aq)

5.1. Entropy

The entropy of Cm^{4+}(aq) can be estimated in a similar manner as that of Cm^{3+}(aq) (Fig. 6). However, the basis for the estimation is considerably less certain as no comparison with the lanthanides can be made. It must be based on the limited number of data for the An^{4+} aqueous ions only.

We here assumed that the variation in the actinide series is mainly due to the excess contribution S_{exs} from the changes in electronic configuration, which is

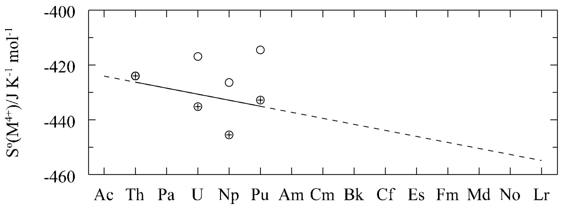

Fig. 6. The variation of $S°(298.15\ K)$ for actinide(IV) aqueous ions. The values indicated by ○ are the experimental values, those indicated by ⊕ are the values $S_{exp} - S_{exs}$. The line represents a linear fit through the data points for Th^{4+}, U^{4+} and Pu^{4+}.

Table 2
The enthalpy of solution of Cm(cr) in HCl(aq)

Refs.	Year	Molarity	$\Delta_{sln}H°/kJ\ mol^{-1}$
[32]	1966	1.0	-585.3 ± 4.2[a]
[33]	1965	1.0	-586.2 ± 4.2
[31]	1969	1.0	-603 ± 12[b]
[30]	1975	1.0	-614.5 ± 4.5
[34]	1981	1.0	-606.5 ± 6.0[c]
		6.0	-602.4
Selected value			-614.5 ± 6.0

[a] The experimental data reported by Bansal [32] and Wallmann et al. [33] are partially the same.

[b] This value was obtained by Morss using α-assays to recalculate the weight of curium from all measurements made between 1962 and 1965 at UCRL [32,33], and includes new measurements by Morss.

[c] Also reported by Raschella [82].

Table 3
The standard molar entropies of the An^{4+} aqueous ions at 298.15 K, in J K^{-1} mol^{-1}

	state	S_{exs}	S_{exp}	$S_{exp} - S_{exs}$	S_{est}	Refs.
Th^{4+}	$^1S_0$	0.00	-424.0 ± 3.6	−424.0	−426	[38]
Pa^{4+}	$^2F_{5/2}$	14.90			−414	–
U^{4+}	$^3H_4$	18.27	-416.9 ± 12.6	−435.2	−412	[22]
Np^{4+}	$^4H_{9/2}$	19.14	-426.4 ± 12.4	−445.5	−414	[23]
Pu^{4+}	$^5I_4$	18.27	-414.5 ± 10.2	−432.8	−417	[23]
Am^{4+}	$^6H_{5/2}$	14.90			−422	–
Cm^{4+}	$^7F_0$	0.00			−439	–

S_{exs} is the excess value calculated from the ground state degeneracy, S_{exp} the experimental value and S_{est} the estimated value, as descibed in the text.

superimposed on a linear change in the actinide series, as was observed for the Ln^{3+} series. Because the ground-state degeneracy of the Cm^{4+} ion is $^7F_0$, S_{exs} is zero, like is the case for Th^{4+}. In a first approximation $S^\circ(Cm^{4+}, aq, 298.15 K)$ is thus about equal to $S^\circ(Th^{4+}$, aq, 298.15 K). Morss and McCue [38] derived for the latter the value $-(424.0 \pm 3.6)$ J K^{-1} mol^{-1}. Alternatively, one can derive the base level by subtracting S_{exs} from the experimental values for U^{4+}, Np^{4+} and Pu^{4+} (see Table 3). The values for Th^{4+}, U^{4+} and Pu^{4+} form approximately a straight line, as one would expect on the basis of the data for the trivalent ions; Np^{4+} deviated considerably from this trend. The entropy of Cm^{4+} is obtained by extrapolation of this trend as

$$S^\circ(Cm^{4+}, aq, 298.15\ K) = -(439 \pm 15)\ J\ K^{-1}\ mol^{-1}. \tag{14}$$

David et al. [27–29] estimated $S^\circ(Cm^{4+}, aq, 298.15\ K) = -408$ J K^{-1} mol^{-1}, using the approach described under Cm^{3+}. However, their calculations did not take into account the experimental data for U^{4+}, Np^{4+} and Pu^{4+}. Moreover, the value they obtained for Pu^{4+}, −399 J K^{-1} mol^{-1}, is not consistent with the experimental result [23].

5.2. Enthalpy of formation

A method to derive the enthalpy of formation of Cm^{4+}(aq) was presented by Morss and Fuger [39,40]. They estimated for the reaction

$$CmO_2(cr) + 4H^+(aq) = Cm^{4+}(aq) + 2H_2O(l). \tag{15}$$

$\Delta_rH^\circ(298.15\ K) = -(40 \pm 7)$ kJ mol^{-1}, using data on other actinide and lanthanide MO_2(cr) and M^{4+}(aq) species, and assuming a linear relation between $\Delta_rH^\circ(298.15\ K)$ and the MO_2 unit cell length. Combining this value with the selected enthalpy of formation of CmO_2 (see below), the enthalpy of formation of Cm^{4+} is derived as

$$\Delta_fH^\circ(Cm^{4+}, aq, 298.15\ K) = -(380 \pm 10)\ kJ\ mol^{-1}. \tag{16}$$

The selected data correspond to a standard potential $E^0 = -3.0$ V of the Cm^{3+}/Cm^{4+} couple, which is in good agreement with the value $-3.1/-3.2$ V derived by Nugent et al. [41] from experimental information on the properties of lanthanide and actinide chlorocomplexes.

6. Cm^{2+}(aq)

Data for the Cm^{2+} aqueous ion are very limited and the experimental basis for estimating the thermodynamic properties of this species is poor. David [29] estimated the standard entropy $S^\circ(Cm^{2+}, aq, 298.15\ K) = -5.9$ J K^{-1} mol^{-1}, using the approach described under Cm^{3+} (Eq. (11)). Morss [42] obtained $S^\circ(Cm^{2+}$, aq, 298.15 K) = −1 J K^{-1} mol^{-1}, using a comparable approach, which we select here. Silva et al. [11] estimated the uncertainty of this method as ±15.

$$S^\circ(Cm^{2+}, aq, 298.15\ K) = -(1 \pm 15)\ J\ K^{-1}\ mol^{-1}. \tag{17}$$

Spitsyn et al. [43] measured the standard potential of the Cm^{3+}/Cm^{2+} couple ($E^0 = -2.78 \pm 0.07$ V). The experimental value is lower than the estimates −3.3 V by Bratsch and Lagowski [44] and −4.4 V by Nugent [45,46]. Because the experimental value is not without doubt, we select the mean of three values, resulting in

$$\Delta_fH^\circ(Cm^{2+}, aq, 298.15\ K) = -(240 \pm 40)\ kJ\ mol^{-1}. \tag{18}$$

In view of the uncertainties, these values need to be considered as approximations.

7. The curium–oxygen phase diagram

The sesquioxide and dioxide were the first phases to be identified in the curium–oxygen system [47,48]. The dioxide has a fluorite type structure like the other actinide dioxides, the lower composition limit being O/Cm = 1.97 for $^{244}CmO_{2-x}$ [49]. CmO_2 is stable to 653 K [49]. Above that temperature it decomposes via two intermediate compositions to Cm_2O_3 [49–51]. Chikalla and Eyring [51] concluded from oxygen-dissociation pressure measurements that the compositions of these intermediate phases are $CmO_{1.82}$ and $CmO_{1.72}$, the former showing a composition range O/Cm between 1.821 and 1.849. They also observed an additional non-stoichiometry near the dioxide and sequioxide compositions. These observations were confirmed by Mosley [49] by combined thermogravimetric and X-ray diffraction measurements. He observed the following features:

- $CmO_{1.81}$ has a fluorite cubic structure with a narrow range of composition. This phase is stable up to 748 K. Above this temperature it decomposes to $CmO_{1.76}$ at 773 K and $CmO_{1.72}$ at 973 K.
- $CmO_{1.72}(Cm_7O_{12})$ was found to have a rhombohedral structure resulting from a small distortion from the fluorite fcc structure, the composition O/M ranging from 1.72 to 1.76.
- A bcc phase exits between Cm_2O_3 and $CmO_{1.72}$ with a variable composition O/M between 1.52 and 1.64 (analogue to the σ phase of the lanthanide sesquioxides). This phase is also formed when $CmO_{1.72}$ is heated above 973 K. Above 1273 K only B-type Cm_2O_3 is stable.

Several crystal structures of the sesquioxide have been reported for the sesquioxide to exist at room temperature, similar to the structural behaviour of the lighter rare-earth sesquioxides: cubic (C-type), monoclinic (B-type) and hexagonal (A-type). The cubic form transforms irreversibly to the monoclinic form near 1273 K [49]. Mosley [49] has suggested that this transformation is accompanied by a small weight loss, suggesting that the B-type is the stoichiometric sequioxide. The effect of self-irradiation resulting from α-decay causes the cubic C-form to transform into the hexagonal A-form, as observed by Wallmann [52] and Haug [53] whereas Mosley [54] observed a spontaneous transformation to the monoclinic B-form at room temperature, when significantly larger quantities of material were used. On the basis of this information Smith and Peterson [55] suggested a phase diagram for atmospheric conditions.

Sudakov et al. [56–58] studied the phases in the $CmO_{1.5}$–CmO_2 region by high-temperature X-ray diffraction and quenching experiments. Their results confirmed many of the results of the US work for CmO_2 and Cm_2O_3. However, these authors proposed the existence of two additional phases in the $CmO_{1.5}$–$CmO_{1.71}$ region: a tetragonal phase stable between 523 and 723 K and a rhombohedral phase stable between 773 and 1073 K. Both are related to the fluorite structure. They estimated the compositions of the phases to be O/M 1.65–1.70 and O/M 1.60–1.65, respectively. These phases become amorphous when stored at room temperature, followed a recrystallisation to $CmO_{1.71}$. Sudakov et al. suggested that radiation damage may play a role in the formation of these phases but excluded an effect of the addition of the diluent (SiO_2) that was added to the powder.

All these studies were made with ^{244}Cm. Turcotte et al. [59], however, repeated the oxygen dissociation pressure measurements of Chikalla and Eyring [51] using ^{248}Cm, for which the α activity is about 2×10^4 less, hence, reducing significantly the effect of radiation damage. They observed no gross differences between the phase relations using ^{244}Cm or ^{248}Cm, but the temperature and composition ranges of the various compounds are somewhat different:

- $^{248}CmO_{2-x}$ has a lower composition limit of $O/Cm = 1.92$–1.94, and an upper composition limit of $O/Cm = 1.99$ and a somewhat higher thermal stability than $^{244}CmO_{2-x}$ (∼50 K). As a consequence, the $CmO_{1.82}$ phase is stable in a smaller temperature range.
- The $CmO_{1.72}$–$CmO_{1.82}$ phase boundary is shifted to a higher temperature.
- The $^{248}CmO_{1.72}$ phase has a very narrow composition ($\Delta(O/M) < 0.001$). It decomposes to $CmO_{1.5+x}$.
- The $CmO_{1.5+x}$ phase (σ) becomes unstable with respect to Cm_2O_3 at 1138 K.
- $^{248}Cm_2O_3$ does not oxidise above 793 K.

A tentative phase diagram for the $CmO_{1.5}$–CmO_2 system is given in Fig. 7. The observations of Sudakov et al. [58] are not included in view of the many unre-

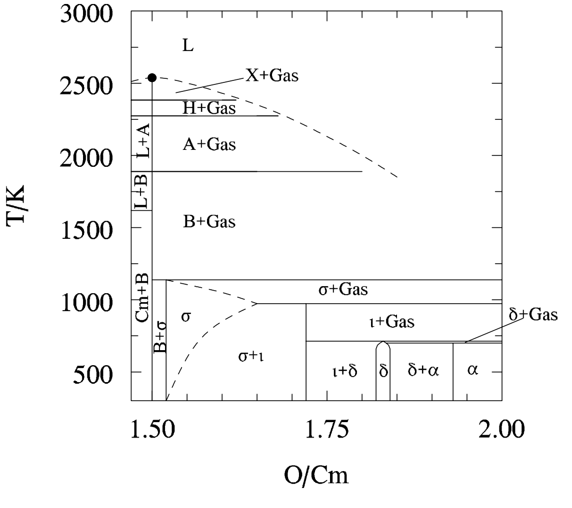

Fig. 7. The curium–oxygen phase diagram in the region $CmO_{1.5}$–CmO_2 (p_{O_2} = 0.2 bar), modified after Smith and Peterson [55]: $\alpha = CmO_{2-x}$, $\delta = CmO_{1.83}$, $\iota = CmO_{1.71}$, $\sigma = CmO_{1.5+x}$(bcc), B = $CmO_{1.5}$(mon), A = $CmO_{1.5}$(hex), H and X are high-temperature structure types.

Table 4
Lattice constants of the phases in the curium–oxygen system

Phase	Structure	Cell parameters		Space group	Refs.
		Axes/pm	Angles/deg		
α-Cm	Hexagonal	$a = 349.6(3)$ $c = 1133.1(5)$		$P6_3/mmc$	[8][a]
β-Cm	Cubic	$a = 503.9(2)$		$Fm\bar{3}m$	[4][a]
CmO_2	Cubic	$a = 535.9(2)$		$Fm\bar{3}m$	[83][a]
$CmO_{1.81}$	Cubic	$a = 543.5(1)$			[49][b]
$CmO_{1.72}$	Rhombohedral	$a = 667.7(4)$	$\alpha = 99.52(7)$		[49][b]
A-Cm_2O_3	Hexagonal	$a = 379.9(2)$ $c = 598.7(4)$		$P\bar{3}m1$	[84][b]
B-Cm_2O_3	Monoclinic	$a = 1428.2(9)$ $b = 364.1(3)$ $c = 888.3(8)$	$\beta = 100.29(7)$	C2/m	[84][b]
C-Cm_2O_3	Cubic	$a = 1100.17(12)$		$Ia\bar{3}$	[84][b]

[a] ^{248}Cm isotope.
[b] ^{244}Cm isotope; results refer to zero radiation damage.

solved questions related to this work. The crystallographic properties of the curium oxide phases are summarised in Table 4.

8. Cm_2O_3(cr)

8.1. Phase transformations and melting point

The stoichiometric sequioxide has a monoclinic crystal structure at room temperature as discussed in the previous section. Upon heating, three high-temperature transformations have been identified by Gibby et al. [60,61]. At (1888 ± 15) K the monoclinic form transforms into the A-type hexagonal structure, as was also observed by high-temperature X-ray diffraction [49]. Above 2000 K transitions at (2273 ± 20) K and at (2383 ± 20) K have been observed, which are most likely transformations to the H and X structures that are known for the lanthanide sesquioxides (H = hexagonal, X = unknown).

There are several reports of the melting point of Cm_2O_3, as summarised in Table 5. The values are in good agreement, except the results of McHenry [62], who used CmO_2 as starting material and assumed that it was converted to the sesquioxide during the measurements. Though no specific reference has been made except for the study of Smith [63], we presume that the measurements refer to the IPTS-48 temperature scale. This means that a small correction of +3 K to the ITS-90 temperature scale is needed [10]. Smith [63] used the melting points of Al_2O_3 and Tm_2O_3 as reference. For the former, a value about 7 K lower than the currently accepted value was obtained. For Tm_2O_3 no recommended value is available. We correct the value by Smith therefore with +7 K. The selected value for the melting point is $T_{fus} = (2543 \pm 25)$ K.

8.2. Heat capacity and entropy

The low-temperature heat capacity of Cm_2O_3 has not been measured but several estimates have been made. Westrum and Grønvold [64] have estimated for the value $S°(298.15\ K) = 160.7\ J\ K^{-1}\ mol^{-1}$ (specified as cubic), by describing the entropy as the sum of the lattice entropy and an excess contribution. A similar approach,

Table 5
The melting point of Cm_2O_3(s)

Refs.	Year	Method[a]	T_{fus}/K	
			Reported	Corrected[b]
[62]	1965	O	2223	
[63]	1969	O	2538 ± 20	2545 ± 20
[60,61]	1970	O	2548 ± 25	2551 ± 25
		DTA	2538	2541
[85]	1973	O	2533 ± 20	2536 ± 20
Selected value				2543 ± 25

[a] O = optical observation during heating in controlled atmosphere; DTA = differential thermal analysis.
[b] ITS-90.

but using a more sound basis of spectroscopic and calorimetric information, was used by Konings [65] who obtained (167.0 ± 5.0) J K^{-1} mol^{-1} without specifying the crystallographic modification, as no such effect was evident for the lanthanide sesquioxides. The value was composed of a lattice part (132.4 J K^{-1} mol^{-1}), obtained by extrapolating the trend in the lanthanide sesquioxides to the actinide sesquioxides, and an excess part (34.58 J K^{-1} mol^{-1}), calculated from the ground state degeneracy of the Cm^{3+} ion. This value is accepted here:

$$S^\circ(\mathrm{Cm_2O_3, cr, 298.15\ K}) = (167.0 \pm 5.0)\ \mathrm{J\ K^{-1}\ mol^{-1}}. \tag{19}$$

Estimated values for the high-temperature heat capacity of monoclinic Cm_2O_3 have been presented by Gibby et al. [60], who used them to convert the thermal diffusivity measurements to thermal conductivity data, which agree reasonably with direct measurements (see below). However, Gibby's values are rather high compared to the experimental values for the lanthanide sesquioxides [12] and Pu_2O_3 [66]. At 298.15 K the extrapolated value of Gibby's estimates is 133.7 J K^{-1} mol^{-1}. The value for the lanthanide analogue Gd_2O_3(monoclinic) [67] is 105.52 J K^{-1} mol^{-1} at 298.15 K. Because in both compounds the excess heat capacity due to crystal field splitting or low-lying excited electronic levels can be neglected, these values are identical to the lattice heat capacity. The heat capacity at 298.15 K of hexagonal Pu_2O_3 is 116.98 J K^{-1} mol^{-1} [66], which yields a lattice heat capacity of $C_{\mathrm{lat}} = 114.3$ J K^{-1} mol^{-1} ($C_{\mathrm{exs}} =$ 2.68J K^{-1} mol^{-1} as calculated from the crystal field levels). For the lanthanide sesquioxides C_{lat} (298.15 K) linearly decreases along the series, irrespective of the crystal structure (hexagonal, monoclinic and cubic), as shown in Fig. 8.

Based on these considerations, we estimate the heat capacity of monoclinic Cm_2O_3 by multiplying the heat capacity of monoclinic Gd_2O_3 (obtained by fitting the experimental results in [67,68]) by the ratio of the lattice heat capacities at 298.15 K of Pu_2O_3 and Sm_2O_3. We thus obtain (298.15–1888 K)

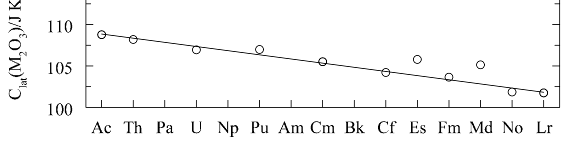

Fig. 8. The variation of C_{lat}(298.15 K) in the lanthanide sesquioxide series (○) and the value for Pu_2O_3 (●). The line connects the values for La_2O_3, Gd_2O_3 and Lu_2O_3 for which C_{exs} is zero at 298.15 K.

$$C_p(\mathrm{Cm_2O_3, cr}, T)/\mathrm{J\ K^{-1}\ mol^{-1}} = 123.532 + 14.550 \times 10^{-3}(T/\mathrm{K}) - 1.3489 \times 10^{6}(T/\mathrm{K})^{-2}. \tag{20}$$

Data on the heat capacity of the H, X and liquid (L) phases and enthalpies of transition for C → H, H → X, and X → L are not available. Since such data are also not existing for the lanthanide sequioxides, an estimation would be rather speculative.

8.3. Enthalpy of formation

The enthalpy of solution of monoclinic curium sesquioxide in 6 mol dm^{-3} HCl(aq) has been measured by Morss et al. [69] by solution calorimetry using milligram samples of the monoclinic form. We combine this result with the enthalpy of solution of Cm metal in this solvent, estimated from the value for the dissolution in 1.0 mol dm^{-3} HCl(aq), and obtain for the enthalpy of formation (see Table 6)

$$\Delta_f H^\circ(\mathrm{Cm_2O_3, cr, 298.15\ K}) = -(1684 \pm 14)\ \mathrm{kJ\ mol^{-1}}. \tag{21}$$

8.4. Thermal expansion

The linear thermal expansion of monoclinic Cm_2O_3 has been measured by Mosley [49] up to about 1700 K by X-ray diffraction. The results, which were only presented in graphical form, can be represented by the equation

$$\Delta L/L_0 = -0.1646 + 4.4449 \times 10^{-4}(T/\mathrm{K}) + 3.6066 \times 10^{-7}(T/\mathrm{K})^2, \tag{22}$$

where $\Delta L/L_0$ is the linear thermal expansion (in %). ΔL is zero at 298 K.

8.5. Thermal conductivity

The thermal conductivity of monoclinic curium sesquioxide has been measured by Ketchen [70] and Gibby et al. [60]. Ketchen made measurements in the 773–1373 K range using a direct technique, in which the alpha decay of ^{244}Cm served as the heat source. The sample contained 5% Cm isotopes other than ^{244}Cm, about 2 wt% Pu, and Am and Zr between 0.4 and 0.9 wt%. The results show a slight decrease with increasing temperature (Fig. 9). Gibby et al. measured the thermal diffusivity of $^{244}Cm_2O_3$ with a laser-pulse method in the 373–1723 K range on a sample with a metal content of 93% Cm and 4% Pu, containing Ca and Mg as major impurities (0.5 wt%). The thermal conductivity was calculated from these data using an estimated heat capacity equation. The data thus obtained by Gibby et al. indicate that the thermal conductivity of Cm_2O_3 is constant in the

Table 6
The standard molar enthalpies of formation of the curium oxides

Reaction	$\Delta_r H°(298.15\ \mathrm{K})/\mathrm{kJ\ mol^{-1}}$
$Cm_2O_3(cr)$	
1. $Cm_2O_3(cr) + 6HCl(sln) = 2CmCl_3(sln) + 3H_2O(sln)$	-400.0 ± 5.0[a]
2. $2Cm(cr) + 6HCl(aq) = 2CmCl_3(sln) + 3H_2(g)$	-1224.0 ± 13.0[b]
3. $3H_2(g) + \frac{3}{2}O_2(g) = 3H_2O(sln)$	-859.93 ± 0.12[c]
4. $2Cm(cr) + \frac{3}{2}O_2(g) = Cm_2O_3(cr)$	-1683.9 ± 13.9[d]
$CmO_2(cr)$	
1. $CmO_2(cr) + 4H^+(sln) + \frac{3}{2}I^-(sln) = Cm^{3+}(sln) + \frac{1}{2}I_3^-(sln) + 2H_2O(sln)$	-215.0 ± 2.10[e]
2. $\frac{3}{4}H_2(g) + \frac{3}{4}I_2(cr) = \frac{3}{2}I^-(sln) + \frac{3}{2}H^+(sln)$	-85.17 ± 0.08[f]
3. $\frac{3}{4}I_2(cr) + \frac{1}{4}H_2(g) = \frac{1}{2}I_3^-(sln) + \frac{1}{2}H^+(sln)$	-25.90 ± 0.25[g]
4. $Cm(cr) + 3H^+(sln) = Cm^{3+}(sln) + \frac{3}{2}H_2(g)$	-614.7 ± 6.5[h]
5. $2H_2(g) + O_2(g) = H_2O(sln)$	-571.67 ± 0.08[i]
6. $Cm(cr) + O_2(g) = CmO_2(cr)$	-912.1 ± 6.8[j]

[a] [69].

[b] Derived from the assessed enthalpy of solution of Cm(cr) in 1 mol dm^{-1} HCl(aq) by adding +3.0kJ mol^{-1}, which is the difference between the enthalpies of solution of Am(cr) in 1.0 and 6.0 mol dm^{-1} HCl(aq) [35].

[c] The partial molar enthalpy of formation of HCl(aq).

[d] $\Delta_r H°(4) = -\Delta_r H°(1) + \Delta_r H°(2) + \Delta_r H°(3)$.

[e] The value given by Morss et al. [40,78] corrected for the 'transfer' from $H_2SO_4(aq)$ to HCl(aq) as given by Morss and Fuger [39] for the Am case.

[f] Calculated with $\Delta_f H°(I^-, aq, 298.15\ K)$ from [71], following Morss and Fuger [39].

[g] Calculated with $\Delta_f H°(I_3^-, aq, 298.15\ K)$ following Morss and Fuger [39].

[h] Derived from the assessed enthalpy of solution of Cm(cr) in 1 mol dm^{-1} HCl(aq), assuming the difference between the enthalpies of solution in 1.0 and 0.55 mol dm^{-1} HCl(aq) to be 0.2 kJ mol^{-1}, as extrapolated from the results for Am(cr) [35].

[i] The partial molar enthalpy of formation of $H_2O(aq)$.

[j] $\Delta_r H°(6) = -\Delta_r H°(1) - \Delta_r H°(2) + \Delta_r H°(3) + \Delta_r H°(4) + \Delta_r H°(5)$.

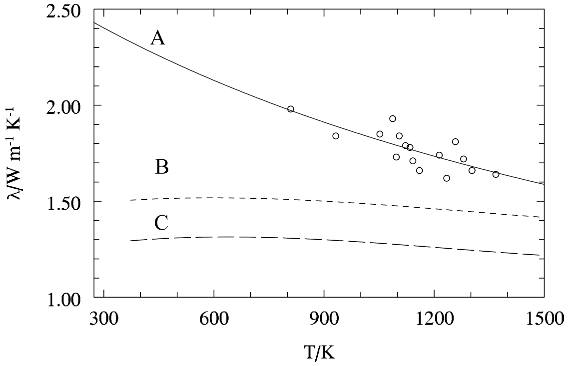

Fig. 9. The thermal conductivity of Cm_2O_3: ○ [70], curve A represents the recommended fit of the results of Ketchen, curve B represents the original data of Gibby et al. [60], and curve C the results of Gibby et al., recalculated with the heat capacity equation selected in this work.

temperature range of the measurements (between 1.53 and 1.65 W m^{-1} K^{-1}) and approach the results of Ketchen above 1100 K (Fig. 9). However, the heat capacity data used by Gibby et al. should be considered too high, as discussed above. When the results are re-calculated with the heat capacity equation selected here, the agreement is no longer evident: the results are about 20% lower (λ is between 1.32 and 1.20 W m^{-1} K^{-1}).

It is well known that radiation damage from α-decay has a significant effect on the thermal conductivity by the creation of crystal defects. These defects can be annealed by a high-temperature treatment, generally above 1300–1400 K though Mosley [49] suggests a temperature of about 723 K. For that reason Ketchen [70] heated the sample above 1273 K in the initial measurement. Gibby et al. [60] recorded the thermal diffusivity during heating and cooling, observing that the initial values in the first run increased abruptly at 673 K, which they attributed to annealing effects. Since further details of the measurements are lacking, it is difficult to assess the magnitude of the effect of radiation damage in the two studies. We here assign a higher confidence to the data of Ketchen, which are not affected by uncertainties in the heat capacity, and which are more carefully treated to minimise the effect of radiation damage. The results of Ketchen have been fitted to the equation

$$\lambda/\mathrm{W\ m^{-1}\ K^{-1}} = \frac{1}{(0.3629 + 1.78 \times 10^{-4}(T/\mathrm{K}))}. \qquad (23)$$

8.6. Vapourisation behaviour

Smith and Peterson [55] have measured the vapourisation of Cm_2O_3 by the Knudsen effusion technique and presented convincing evidence that the vapourisation of Cm_2O_3 proceeds according to the reaction

$$Cm_2O_3(cr) = 2CmO(g) + O(g) \tag{24}$$

which is well known from the lanthanide sesquioxides. Smith and Peterson performed four sets of effusion measurements in the 1800–2600 K range, three with W and one with Mo effusion cells, as summarised in Fig. 10. According to the authors only one set of measurements represents the vapour pressure accurately and the results of this set have been fitted to the equation (1843–2609 K)

$$\log(p_E/p^\circ) = (7.334 \pm 0.26) - (29065 \pm 590)(T/\mathrm{K})^{-1}, \tag{25}$$

where p_E is the pressure calculated by Smith and Peterson [55] assuming that 1 mol of gas atoms was present in the vapour phase with the overall composition Cm_2O_3, and p° is the reference pressure 1 atm. This yields for the second-law enthalpy of vapourisation $\Delta_{sub}H^\circ(2225\ \mathrm{K}) = 556.4\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_{sub}S^\circ(2225\ \mathrm{K}) = 140.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$, which then refer to the equilibrium

$$\frac{1}{3}Cm_2O_3(cr) = \frac{2}{3}CmO(g) + \frac{1}{3}O(g). \tag{26}$$

To analyse these measurements in more detail, the molecular properties of CmO(g) have to be estimated. We have assumed a linear molecule with a Cm–O internuclear distance of 179 pm. The vibrational parameters $\omega_e = 820\ \mathrm{cm^{-1}}$ and $\omega_e x_e = 2\ \mathrm{cm^{-1}}$ were assumed to be close to those of UO(g) and the gaseous lanthanide monoxides. The electronic ground state of CmO(g) was taken as $^7F_6$; no excited electronic states have been included in the calculations.

Combining the approximate results for CmO(g) thus obtained, with the data for O(g) [71] and Cm_2O_3(cr) (this study) the second-law value is corrected to $\Delta_{sub}H^\circ(298.15K) = 526\ \mathrm{kJ\ mol^{-1}}$. This yields an approximate value for the enthalpy of formation of CmO(g) of $\Delta_f H^\circ(\mathrm{CmO, g, 298.15\ K}) = -175\ \mathrm{kJ\ mol^{-1}}$.

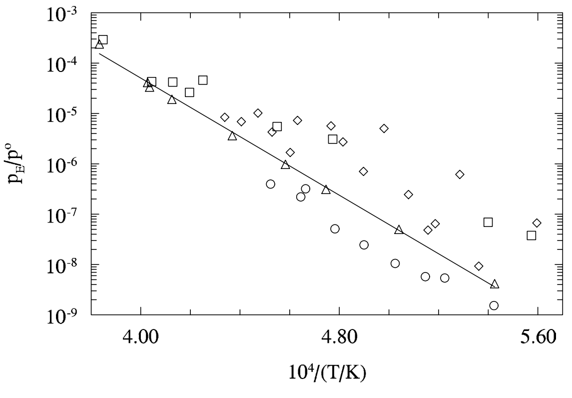

Fig. 10. The vapour pressure p_E/p° of Cm_2O_3 [55]; the symbols indicate the four different experiments that were made using tungsten (○, △, □) and molybdenum effusion cells (◇). The line shows the recommended equation given in the text.

9. CmO_2(cr)

9.1. Phase transformations

Curium dioxide has a fluorite-type crystal structure (space group $Fm\bar{3}m$) at room temperature. Radiation damage from α-decay in $^{244}CmO_2$(cr) results in a rapid change in lattice parameter, and reaches equilibrium after about 3 days (He atmosphere) [72,49,73,74]. The change in the lattice parameter can be described by $\Delta a/a_0 = 2.33 \times 10^{-3}(1 - e^{-1.52\times10^4 \lambda t})$, where λ is the disintegration constant for α-decay in ^{244}Cm ($4.37 \times 10^{-6}\ \mathrm{h^{-1}}$) and t is time [73].

As discussed before, CmO_2 is stable up to 700 K. Above that temperature it is reduced to $CmO_{1.95}$, followed by rapid decomposition via the various intermediate oxides to Cm_2O_3.

9.2. Heat capacity and entropy

The low-temperature heat capacity of CmO_2 has not been measured. Westrum and Grønvold [64] estimated $S^\circ(298.15\ \mathrm{K}) = 87.4\ \mathrm{J\ K^{-1}\ mol^{-1}}$ in the early 1960s, by describing the entropy as the sum of the lattice entropy and an excess (magnetic) contribution, $S_{lat} = 71.1\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $S_{exs} = 16.3\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The value for S_{lat} seems to be too high when one considers that the same value was used by Westrum and Grønvold for the other actinide dioxides. However, the experimental values for ThO_2, for which the excess contribution is zero, and PuO_2 for which the excess contribution is $1.55\mathrm{J\ K^{-1}\ mol^{-1}}$ (see Table 7), are $65.23\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $66.78\ \mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. If CmO_2 has a non-degenerate ground state, as often suggested, S_{exs} is zero and the standard entropy of CmO_2 is close to that of ThO_2. However, Morss et al. [75] concluded from magnetic susceptibility measurements, which indicate that the average value μ_{eff} for stoichiometric CmO_2 is not zero but $(3.36 \pm 0.06)\mu_B$, that this may not be true. Up to now it has not been resolved whether this observation is due to experimental artefacts (Cm^{3+} impurity in an amorphous phase which was not detected) or to a not-yet-understood physical feature of CmO_2. For this work we select the value

$$S^\circ(\mathrm{CmO_2, cr, 298.15\ K}) = (65 \pm 5)\ \mathrm{J\ K^{-1}\ mol^{-1}}. \tag{27}$$

For similar reasons the heat capacity of CmO_2(cr) has been assumed to be the sum of that of ThO_2 between 300 and 650 K [76] and a small excess contribution derived

Table 7
The standard molar entropies of the actinide dioxides, assuming S_{lat} to be identical to that of ThO_2; in J K^{-1} mol^{-1}

	S_{lat}	S_{exs}[a]	S_{tot}	S_{exp}	Refs.
ThO_2	65.23	0.00	65.23	65.23 ± 0.20	[71]
UO_2		9.34	74.57	77.03 ± 0.20	[71]
NpO_2		14.15	79.38	80.30 ± 0.40	[23]
PuO_2		1.55	66.78	66.13 ± 0.26	[23]
AmO_2		12.46	77.70		
CmO_2		0.00	65.23		

[a] Calculated from the crystal field energy levels given by Krupa and Gajek [86] for UO_2, NpO_2 and PuO_2. For AmO_2 the crystal field energy levels have been calculated by Krupa [77] to be 0(2), 328(4) cm^{-1}; the ground state of CmO_2 was taken as non-degenerate [77].

from the energy levels of CmO_2 calculated by Krupa [77]. It is represented by the equation

$$C_p(\mathrm{CmO_2, cr}, T)/\mathrm{J\,K^{-1}\,mol^{-1}} = 64.871 + 19.152 \times 10^{-3}(T/\mathrm{K}) - 7.860 \times 10^{5}(T/\mathrm{K})^{-2}. \qquad (28)$$

9.3. Enthalpy of formation

The enthalpy of formation of CmO_2 has been derived by Morss [40,78] from solution calorimetry measurements in (0.5 mol dm^{-3} H_2SO_4 + 0.1 mol dm^{-3} KI) solution for samples with composition $CmO_{2.00}$ and $CmO_{1.93}$. The results for the two samples, when the latter is corrected to O/M = 2.00, are in good agreement: $\Delta_{\mathrm{sln}}H^\circ(298.15\ \mathrm{K}) = -(223.6 \pm 2.1)\ \mathrm{kJ\,mol^{-1}}$ and $-(225 \pm 6)\ \mathrm{kJ\,mol^{-1}}$, respectively. When the thermochemical cycle for the $CmO_{2.00}$ sample is recalculated with the most recent auxiliary data (see Table 6) and assuming that the enthalpies of mixing of $CmCl_3$, HCl and H_2SO_4 solutions are the same as for the Am case [39], we obtain

$$\Delta_f H^\circ(\mathrm{CmO_2, cr}, 298.15\ \mathrm{K}) = -(912.1 \pm 6.8)\ \mathrm{kJ\,mol^{-1}}. \qquad (29)$$

Morss also reported measurements for $CmO_{1.986}$ and $CmO_{1.982}$ in (6.0 mol dm^{-1} HNO_3 + 0.1 mol dm^{-1} $NaBF_4$) solution but these results have not been used.

9.4. Thermal expansion

The linear thermal expansion of monoclinic $^{244}CmO_2$ has been measured by Mosley [49] between room temperature and 713 K by X-ray diffraction. The results, not reported in detail, were described by a linear relation with $\alpha_c = 8.1 \times 10^{-6}\ \mathrm{K^{-1}}$. Noé and Peterson [73] measured the linear thermal expansion of two samples of $^{248}CmO_2$, obtaining $\alpha = (10.10 \pm 0.35) \times 10^{-6}\ \mathrm{K^{-1}}$ (298–733 K) and $\alpha = (10.58 \pm 0.63) \times 10^{-6}\ \mathrm{K^{-1}}$ (293–713 K). The latter two values are in excellent agreement and are preferred to the results of Mosley. From the combined data we derive for the linear thermal expansion (298–650 K)

$$\Delta L/L_0 = -0.3027 + 10.16 \times 10^{-4}(T/K). \qquad (30)$$

where $\Delta L/L_0$ is the linear thermal expansion (in %). ΔL is zero at 298 K.

9.5. Thermal conductivity

The thermal conductivity of CmO_2(cr) has not been measured. Moreover, it is not easy to extrapolate it from the lighter actinide dioxides as the trend in the series is not obvious, mainly due to the remarkably low experimental value for AmO_2 ($\lambda(333\ \mathrm{K}) = 0.69\ \mathrm{W\,m^{-1}\,K^{-1}}$) reported by Schmidt [79]. Bakker and Konings [80] suggested for AmO_2 a value $\lambda(333\ \mathrm{K}) = 6.7$–$9.4\ \mathrm{W\,m^{-1}\,K^{-1}}$, based on a semi-empirical approach suggested by Gibby [81]. Using a comparable approach, we obtain $\lambda(298.15\ \mathrm{K}) = (7$–$10)\ \mathrm{W\,m^{-1}\,K^{-1}}$ and $\lambda(650\ \mathrm{K}) = (3.8$–$4.6)\ \mathrm{W\,m^{-1}\,K^{-1}}$ for CmO_2. These values should be used as indicative only.

10. Conclusion

In the present paper a consistent set of thermophysical and thermochemical properties of Cm(cr), Cm(g), Cm^{3+}(aq), Cm^{4+}(aq), Cm^{2+}(aq), Cm_2O_3(cr), CmO_2(cr) and CmO(g) has been presented. Because the experimental studies published in literature on which this set could be based are limited, a number of estimates had to be made using semi-empirical models to complement the measurements. These estimates are principally based on the extrapolation of trends in the lanthanide series to the actinide series. In doing so, we have noticed significant differences to earlier reports, notably for entropies and heat capacities. This is also true for the data for some americium compounds that were included in the analysis: the entropy values (S°(298.15 K)) derived in this study for Am^{4+} and AmO_2, together with that for Am_2O_3 presented before [65], differ significantly from the selected data in the recent critical assessment in the NEA-TDP [11].

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