CHAPTER NINETEEN

THERMODYNAMIC PROPERTIES OF ACTINIDES AND ACTINIDE COMPOUNDS

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19.1 INTRODUCTION

The necessity of obtaining accurate thermodynamic quantities for the actinide elements and their compounds was recognized at the outset of the Manhattan Project, when a dedicated team of scientists and engineers initiated the program to exploit nuclear energy for military purposes. Since the end of World War II, both fundamental and applied objectives have motivated a great deal of further study of actinide thermodynamics. This chapter brings together many research papers and critical reviews on this subject. It also seeks to assess, to systematize, and to predict important properties of the actinide elements, ions, and compounds, especially for species in which there is significant interest and for which there is an experimental basis for the prediction.

Many experimental and theoretical studies of thermochemical and thermophysical properties of thorium, uranium, and plutonium species were undertaken by Manhattan Project investigators. Some of these reports appeared in the National Nuclear Energy Series (Seaborg *et al.*, 1949). These papers, and others in the literature through 1956, formed the basis for Table 11.11 *Summary of thermodynamic data for the actinide elements* of the first edition of this work. This table, compiled by J. D. Axe and E. F. Westrum Jr., listed 126 species, of which the properties of 40 were estimates. A fair measure of the progress in actinide thermodynamics is the number of subsequent research papers and reviews.

Two other monumental works, which appeared in 1952, must be mentioned here: the U.S. National Bureau of Standards Circular no. 500 (Rossini *et al.*, 1952) included all known data through uranium, and Latimer's oxidation potentials (Latimer, 1952) included oxidation–reduction data on all actinides through americium. Following the publication of the first edition of this work, with its thermodynamic summary in Table 11.11, the only major reviews of actinide thermodynamics during the decade 1960–69 were the monograph of Rand and Kubaschewski (1963) on uranium, the IAEA panel reports on oxides (IAEA, 1965, 1967) and carbides (Rand, 1968), and long reviews by Rand (1966) and Oetting (1967). However, until the 1970s, the reviews of actinide thermodynamics lagged behind the reports of these measurements themselves.

Critical efforts to compile and to assess actinide thermodynamic properties improved during the 1970s and 1980s. Krestov (1972) prepared an extensive compilation of rare earth and actinide thermochemical properties. Rand (1975) comprehensively and critically reviewed thorium thermodynamics, and the thermodynamics group of the U.S. National Bureau of Standards (Wagman *et al.*, 1981) published the final volume of the Technical Note 270 series, which included the elements actinium through uranium. At nearly the same time the parallel compendium of Glushko *et al.* (1978) was published in the USSR. The most contemporary and thoroughly annotated compilation is the 14-part series issued under the auspices of the International Atomic Energy Agency, *The Chemical Thermodynamics of Actinide Elements and Compounds*, of which ten volumes have been published (Fuger and Oetting, 1976; Oetting *et al.*, 1976; Cordfunke and O'Hare, 1978; Chiotti *et al.*, 1981; Fuger *et al.*, 1983; Flotow *et al.*, 1984; Grønvold *et al.*, 1984; Holley *et al.*, 1984; Hildenbrand *et al.*, 1985; Fuger *et al.*, 1992). The nine volumes of this compilation published before 1986 formed the basis for most of the data in the second edition of this work.

After this 'golden age' of thermodynamics of the actinides a significant decrease in the number of experimental studies occurred during the last two decades, when the programs in many laboratories in the U.S. and Europe faced significant budget reductions. Also the review activities at the IAEA stopped before the series was completed. Fortunately many new review activities in this field started in the 1990s. The Nuclear Energy Agency (NEA) of the OECD initiated a project, the Thermodynamic Database Project (NEA-TDB), with the goal to assess and publish the thermochemical data of those actinides that are highly relevant to waste disposal studies: uranium, neptunium, plutonium, and americium (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001;

Guillaumont *et al.*, 2003). The volumes for these elements, which strongly rely upon the work done in the frame of the IAEA activities, have all been published and a supplement with extensions and corrections has been issued recently (Guillaumont *et al.*, 2003). At the Institute for Transuranium Elements (ITU), a systematic review of lanthanide and actinide elements and compounds was undertaken, with the goal of establishing a web-based information center (Konings, 2004b) focused on high-temperature properties. The results of these two projects form, together with the IAEA series, the basis for the present chapter. The thermodynamic studies on the transactinide elements are restricted to a few experimentally determined adsorption enthalpies of halides of elements 104, 105, and 106 on metal surfaces and quantum chemical calculations. For that reason these elements will not be dealt with in this chapter. The reader is referred to Chapter 14.

19.2 ELEMENTS

19.2.1 Actinides in the condensed phase

A systematic and critical review of the available thermodynamic quantities for the actinide elements was made by Ward *et al.* (1986), which is much more complete than the earlier reviews by Hultgren *et al.* (1973) and Oetting *et al.* (1976). Since then the thermodynamic quantities of some actinide elements were reviewed individually in other compilations. Thorium and uranium were carefully reviewed by the CODATA Workgroup for Key Values for Thermodynamics (Cox *et al.*, 1989) and recommended values for the standard entropy, heat capacity, and enthalpy of sublimation at room temperature were given. Reviews for plutonium and americium were reported by Cordfunke and Konings (1990), for uranium, neptunium, plutonium, and americium by the NEA-TDB Project teams (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003), and for americium and curium by Konings (2001b, 2002). These reviews are essentially based on the same information as the work of Ward *et al.* Because few new measurements have been reported since 1986, the differences in values between these reviews mainly arise from the estimation methods, as explained below.

(a) Entropy

The low-temperature heat capacities have been measured for the actinides Th through Am. The experimental measurements were reviewed by Ward *et al.* (1986). The values given by Ward *et al.* (1986) for the heat capacity and entropy of Pa are based on the estimates of Oetting *et al.* (1976), but thereafter heat capacity measurements were reported by Hall *et al.* (1990) from 10 to 300 K.

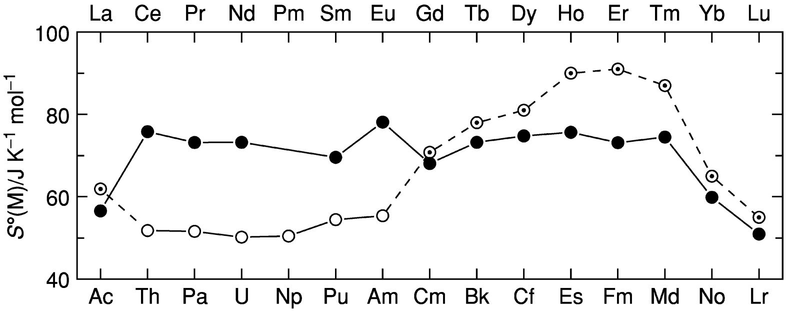

Fig. 19.1 *The standard entropies of lanthanide* (•) *and actinide* (○) *metals at* T = 298.15 K; *estimated values are indicated by* (⊙).

These authors reported preliminary results on several occasions but because the numbers given vary somewhat, the results cited here are from their final report.

The variation of the standard entropies along the actinide metal series is shown in Fig. 19.1. The entropies of the elements Th to Am are below the lattice entropies of the corresponding lanthanides, showing the absence of magnetic contributions. At Cm a distinct increase of the entropy occurs, showing the magnetic character of this element. Konings (2001b) suggested that the entropy of this element can be estimated by adding the excess entropy of Gd to that of Am. Ward and his colleagues (Kleinschmidt *et al.*, 1983; Ward *et al.*, 1986) suggested a more general formula to estimate the entropies of the metals heavier than americium from those of lanthanide and lighter actinide metals by correlation with metallic radius (r), atomic weight (M), and magnetic entropy (S_μ):

$$S_u(298.15\ \mathrm{K}) = S_k(298.15\ \mathrm{K})(r_u/r_k) + \frac{3}{2}R\ \ln(M_u/M_k) + S_\mu \qquad (19.1)$$

where u refers to the unknown element and k to the known element. S_μ is taken equal to $S_{\mathrm{spin}} = (2J + 1)$, where J is the total angular momentum quantum number. The selected values for the entropies of the actinide elements are listed in Table 19.1.

(b) High-temperature properties

High-temperature heat capacity data have only been measured for Th, U, and Pu and the results allow an adequate description of the thermal functions of these elements into the liquid phase. Measurements for Np have only been made up to 480 K (Evans and Mardon, 1959). Oetting *et al.* (1976) and Ward *et al.* (1986) presented estimates for most other actinide metals based on a simple empirical correlation with the lanthanide metals, often adjusted to fit the second- and third-law analysis of the vapor pressure studies. Very similar data for Np and Am were presented in the OECD-NEA project. A semi-empirical

Table 19.1 *Thermodynamic properties of the actinide metals and gaseous elements at* 298.15 K *and* 10^5 Pa*; estimated values are in italics.*

	Crystal		*Gas*			
	C_p(298.15 K) (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	C_p(298.15 K) (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_{sub}H°$(298.15 K) (kJ mol^{-1})	*References*
Ac	*26 ± 2*	*61.9 ± 0.8*	20.817 ± 0.040	188.045 ± 0.10	*418 ± 20*	a
Th	26.23 ± 0.20	51.8 ± 0.5	20.790 ± 0.020	190.17 ± 0.05	602 ± 6	b
Pa	28.2 ± 0.4	51.6 ± 0.8	22.91 ± 0.05	198.11 ± 0.10	570 ± 10	c
U	27.66 ± 0.05	50.20 ± 0.20	23.690 ± 0.020	199.79 ± 0.10	533 ± 8	b
Np	29.62 ± 0.80	50.46 ± 0.80	20.824 ± 0.020	197.719 ± 0.005	465.1 ± 3.0	d
Pu	31.49 ± 0.40	54.46 ± 0.80	20.854 ± 0.010	177.167 ± 0.005	349.0 ± 3.0	d
Am	25.5 ± 1.5	55.4 ± 2.0	20.786 ± 0.010	194.55 ± 0.05	283.8 ± 1.5	d
Cm	*28.8 ± 1.5*	*70.8 ± 3.0*	28.106 ± 0.020	197.5 ± 5.0	384 ± 10	e
Bk		*78 ± 5*	20.786 ± 0.020	200.6 ± 3.0	310 ± 10	f
Cf		*81 ± 5*	20.786 ± 0.020	201.3 ± 3.0	196 ± 10	f
Es		*89 ± 5*	20.786 ± 0.020	201.0 ± 5.0	130 ± 10	f
Fm		*91 ± 5*	20.786 ± 0.020	199.4 ± 5.0	141 ± 13	f
Md		*87 ± 5*	20.786 ± 0.020	195.4 ± 5.0	*141 ± 13*	f
No		*65 ± 5*	20.786 ± 0.020	178.2 ± 5.0	*141 ± 13*	f
Lr		*55 ± 5*	20.786 ± 0.020	184.0 ± 5.0	*341 ± 13*	f

[a] Estimated in this work.
[b] Cox *et al.* (1989).
[c] Ward *et al.* (1986).
[d] NEA-TDB (Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[e] Konings (2001a).
[f] See text.

approach was used by Konings (2003) who presented the heat capacity of α- and β-Am as the sum of the harmonic, anharmonic, dilatation, electronic, and magnetic contributions:

$$C_p = C_{har} + C_{anh} + C_{dil} + C_{ele} + C_{mag} \quad (19.2)$$

This approach gives a good agreement with the low-temperature values; at elevated temperatures the results are somewhat higher than the earlier estimated heat capacity data. Larger differences were found for γ-Am and liquid Am, for which simplified versions of equation (19.2) were used.

Table 19.2 summarizes the transition temperatures and enthalpies for which, again, the data from the above-mentioned reviews have been adopted in most cases. The melting points are plotted in Fig. 19.2 together with those of the lanthanide metals. The melting points in the lanthanide series increase regularly, indicating an increasing cohesive energy in the condensed phase. Eu and Yb form exceptions to this trend as they have a divalent state, whereas the other lanthanides have a predominantly trivalent state. In the actinide series, tetravalent (Th–Pu), trivalent (Ac, Am–Cf, Lr), and divalent (Es–No) states are present, explaining why the melting points of the actinide metals are significantly different from those of the lanthanides. In this context, it is interesting to examine the variation in the sum of the transition entropies of the actinides, shown in Fig. 19.3. Clearly the elements U–Am have a considerably higher value of $\Sigma(\Delta_{trs}S)$ compared to the other actinide metals, for which the values are almost identical to the lanthanide elements. The value for Am is to be discussed in somewhat greater detail (Konings, 2003). The selected values for this element in the NEA-TDB review are based on the work of Wade and Wolf (1967) that was made on massive samples of Am. These values disagree seriously with those of the recent work of Gibson and Haire (1992). However, the values of $\Sigma(\Delta_{trs}S)$ derived from both these studies do not fit the trend suggested by Fig. 19.3. The results of Seleznev *et al.* (1977, 1978) are intermediate between these two studies and $\Sigma(\Delta_{trs}S)$ of Am derived from this work (8.7 J K^{-1} mol^{-1}) fits well in the trend for the trivalent lanthanide metals. Therefore Seleznev's values have been recommended (Konings, 2003). Clearly more work is required for this element.

The trend of the heat capacity of the actinides in the liquid phase is shown in Fig. 19.4 together with that for the liquid lanthanides. The actinides Th–Pu, for which experimental data are available, are tetravalent in the liquid, which explains why the two patterns are different. Am and Cm have a trivalent state, like the lanthanides (except Eu and Yb which are divalent).

The recommended heat capacity functions are summarized in Table 19.2.

19.2.2 Actinides in the gas phase

Heat capacity and entropy of the gaseous actinide elements have been calculated from atomic parameters and electronic energy levels. As discussed by Brewer (1984) the levels for the actinides are complete (through experiments and

Table 19.2 *High-temperature heat capacity of the crystalline and liquid actinide metals;* $C_p/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a(\mathrm{T/K})^{-2} + b + c(\mathrm{T/K}) + d(\mathrm{T/K})^2 + e(\mathrm{T/K})^3$ *(estimated values are in italics).*

		a (×10^{-6})	b	c (×10^{3})	d (×10^{6})	e (×10^{9})	T (K)	$\Delta_{trs}H$ (kJ mol^{-1})	*References*
Ac	α		*25.45*	*−0.584*	*8.095*		*1323 ± 50*	*10.8 ± 2.0*	a
	liq		*35*						a
Th	α		23.435	8.945			1633 ± 20	3.50	b
	β	0.0114	15.70	11.951			2023 ± 10	13.8	b
	liq		46.00						b
Pa	α		21.6522	12.426			1443 ± 20	6.6	c
	β		39.7				1845 ± 20	12.3	c
	liq		47.3						c
U	α		26.9200	−2.5020	26.5558		941 ± 2	2.791	b,d
	β	−0.07699	42.9278				1049 ± 2	4.757	b,d
	γ		38.2836				1408 ± 2	9.142	b,d
	liq		48.660						b,d
Np	α	0.805714	−4.0543	82.555			553 ± 3	5.607 ± 0.500	d
	β		39.33				849 ± 3	5.272 ± 0.500	d
	γ		36.40				912 ± 3	5.188 ± 0.500	d
	liq		45.396						d
Pu	α		18.1258	44.820			397.6 ± 1.0	3.706 ± 0.100	e
	β		27.4160	13.060			487.9 ± 1.0	0.478 ± 0.020	d
	γ		22.0233	22.959			593.1 ± 1.0	0.713 ± 0.040	d
	δ		28.4781	10.807			736.0 ± 2.0	0.084 ± 0.020	d
	δ′		35.560				755.7 ± 2.0	1.841 ± 0.100	d
	ε		33.720				913 ± 2	2.824 ± 0.100	d
	liq		42.248						d
Am	α		30.0399	−29.053	52.026	−18.961	1042 ± 30	0.34 ± 0.08	e
	β		8.4572	33.167	−7.587		1350 ± 5	3.8 ± 0.4	e
	γ		43.0				1449 ± 5	8.0 ± 1.3	e
	liq		52.0						e

Table 19.2 (*Contd.*)

		a ($\times10^{-6}$)	b	c ($\times10^{3}$)	d ($\times10^{6}$)	e ($\times10^{9}$)	T (K)	$\Delta_{trs}H$ (kJ mol^{-1})	*References*
Cm	α		28.409	−0.8284	4.920		*1568 ± 30*	*4.5 ± 0.5*	e
	β		28.3				1619 ± 50	11.7 ± 1.0	e
	liq		37.2						e
Bk	α		27.437	−14.882	21.586		1250 ± 50	3.66	f
	β	0.1059	36.9				1323 ± 50	7.916	f
	liq		42.6						
Cf	α		23.651	9.7865	9.0983		863	2.64	f
	β	0.0580	37.6				1173	7.51	f
	liq		42.5						
Es	α		27.919	4.1825			1133	9.40	f
	liq	−0.2157	37.0						

[a] Estimated in this work.
[b] Cox *et al*. (1989).
[c] Oetting *et al*. (1976).
[d] NEA-TDB (Grenthe *et al*., 1992; Silva *et al*., 1995; Lemire *et al*., 2001; Guillaumont *et al*., 2003).
[e] Konings (2001b, 2003).
[f] Ward *et al*. (1986).

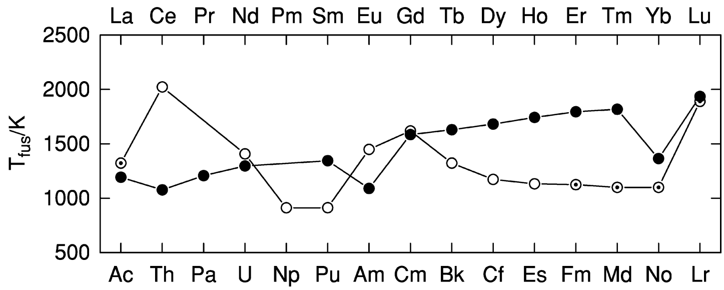

Fig. 19.2 *The melting points of lanthanide* (•) *and actinide* (○) *metals; estimated values are indicated by* (⊙).

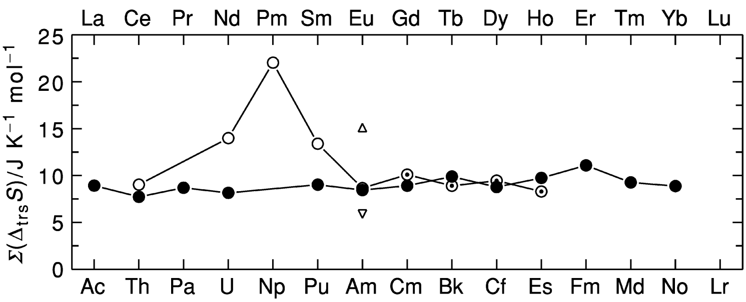

Fig. 19.3 *The sum of the transition entropies of lanthanide* (•) *and actinide* (○) *metals;* ▽, *results for Am from Wade and Wolf* (1967); Δ, *results for Am from Gibson and Haire* (1992)*; estimated values are indicated by* (⊙).

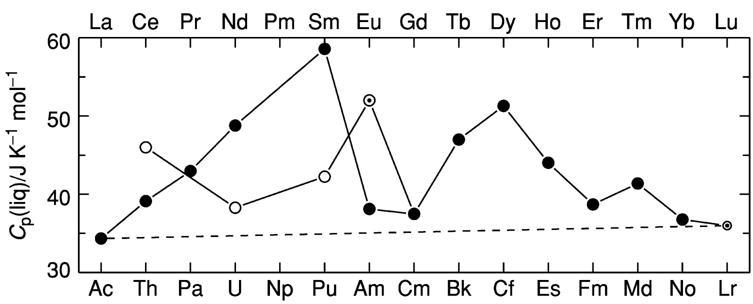

Fig. 19.4 *The heat capacity of the lanthanide* (•) *and actinide* (○) *metals in the liquid state; estimated values are indicated by* (⊙).

estimations) to about 15000 cm^{-1}, which permits the calculation of the values up to about 2000 K with reasonable accuracy. The room temperature values are shown in Table 19.1. The gaseous ions, for which thermodynamic data are also available, are dealt with extensively in Chapter 16 and are excluded from this chapter.

With these data and the thermal functions for the solid, sublimation enthalpies can be derived from the vapor pressure measurements for the actinide elements. Such measurements have been performed for all actinide metals except Md, No, and Lr, though the measurements for Ac (Foster, 1953) are of a very approximate nature. The work performed at Los Alamos and Oak Ridge National Laboratories is noteworthy because these researchers extended the measurements of the transplutonium elements to Cf and finally measured the vapor pressure of Es (Kleinschmidt *et al.*, 1984) and Fm (Haire and Gibson, 1989) using samples containing 10^{-5} to 10^{-7} at% of the actinides in rare earth alloys by applying Henry's law for dilute solutions. The enthalpies of sublimation derived from these studies are listed in Table 19.1. They are plotted in Fig. 19.5 together with the sublimation enthalpies of the lanthanide metals. The trend in the latter series shows a typical pattern, with La, Gd, and Lu forming an approximate linear baseline from which the others systematically deviate. This trend can be understood from the electronic states of the condensed and gaseous atoms, as discussed by Nugent *et al.* (1973), who showed that the difference between the value linearly interpolated in the La–Gd–Lu series and the experimental value corresponds to the energy difference between the lowest electronic energy level of the $f^n s^2 d^1$ configuration and the lowest level of the $f^{n+1} s^2$ configuration. An exception is Eu, which is divalent in the condensed state.

The trend in the actinide series decreases more as a function of Z compared to that for the lanthanides. The explanation for this is found in the complexity of the valence states, as discussed in Section 19.2.2. Several predictions of $\Delta_{sub}H$ for Ac, Md, No, and Lr were made. Nugent *et al.* (1973) correlated energetics of divalent and trivalent lanthanides and actinides. Fournier (1976) correlated

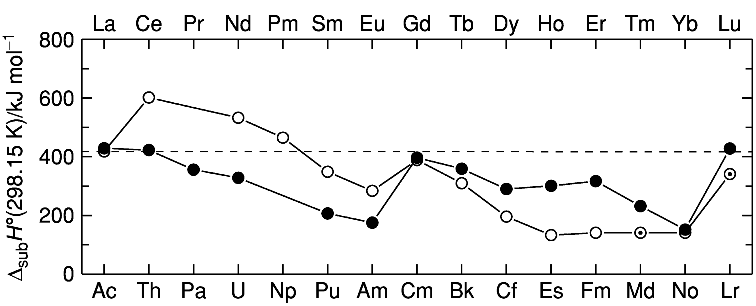

Fig. 19.5 *Enthalpies of sublimation of lanthanide (•) and actinide (○) metals at* $T =$ 298.15 K*; estimated values are indicated by* (⊙).

electronic configuration with metallic radius, melting temperature, and enthalpy of sublimation. A more reliable series of sublimation properties was generated by David *et al.* (1978) and David (1986), who included experimental radio-electrochemical measurements in the correlation. An independent method of estimation of sublimation properties is that of thermochromatography, which has been utilized effectively for the actinides (Hubener and Zvara, 1982). There is general agreement that the enthalpy of sublimation of Lr is in the range 320–350 kJ mol^{-1}, and we select the value estimated by David (1986). His values for Md and No must, however, be considered to be somewhat too high as the estimate for Fm is 32 kJ mol^{-1} higher than the experimental value by Kleinschmidt *et al.* (1984). Fournier estimated the sublimation enthalpies of Fm–No to be approximately the same, as was approximately the case for the results of David. We therefore suggest the same enthalpy of sublimation for Md and No as for Fm. The results are summarized in Table 19.1.

19.3 IONS IN AQUEOUS SOLUTIONS

19.3.1 Enthalpy of formation

For most of the transuranium elements, the enthalpy of formation of aqueous ions were the first thermochemical property to be determined. One reason was that the measurement of the 'heat of solution' of metals or, later, of enthalpies of redox reactions between actinide ions was an appropriate step in the determination of enthalpies of formation of compounds. A more fundamental reason is that the enthalpy of formation of an aqueous ion establishes a fundamental property of that ion and is a reference for all stability studies of compounds of that ion. Because solution microcalorimetry is more readily done than combustion microcalorimetry, milligram-scale enthalpy-of-formation studies of aqueous ions have been possible whereas such studies of oxides and halides by combustion calorimetry have not. In fact, microcalorimetry studies of transuranium elements have been carried out for more than 50 years, with barely an order of magnitude improvement in sensitivity in all that time!

The existing values of actinide aqueous-ion enthalpies of formation of actinium through berkelium were assessed by Fuger and Oetting (1976) in the frame of a series of publications under the auspices of the IAEA (Vienna). More recently, reassessments of the values for the ions of U, Np, Pu, and Am were presented in the NEA-TDB reviews, and for Cm ions by Konings (2001a). For these ions, the new values are preferred to those of Fuger and Oetting. Only in a few instances the differences are significant. For the quadrivalent (and pentavalent) Pa aqueous species, the values accepted here are very marginally different from those recommended by Fuger and Oetting, because of the later measurements with metal samples in the standard body-centered tetragonal form (Fuger *et al.*, 1978) instead of a quenched face-centered cubic form. For berkelium and californium, newer measurements (Fuger *et al.*, 1981, 1984) have provided the tabulated enthalpies of formation. All An^{3+} values are plotted in Fig. 19.6, together with the Ln^{3+} values. The latter vary smoothly within a small band, with exception of Eu^{3+} and Yb^{3+}. These two metals are divalent in the crystal state, whereas the other lanthanide metals are trivalent. In the actinide series the electronic structure is more complex, as discussed in the previous sections, leading to a much more irregular pattern.

An important correlation between trivalent f-block ions and their 'trivalent' atoms ($f^n ds^2$) is the promotion energy function *P*(*M*) proposed by Nugent *et al.* (1973), who utilized it for predicting enthalpies of formation of aqueous ions systematically (Fig. 19.7). David (1986) used the heavy actinide thermodynamic properties to establish a *P*(*M*) function relating all of the actinide metals and their 3+ aqueous ions. Morss and Sonnenberger (1985) used newer data to

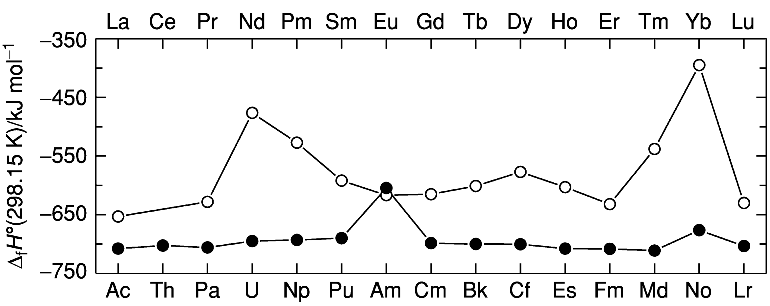

Fig. 19.6 *The enthalpy of formation of the lanthanide* (•) *and actinide* (○) *trivalent aqueous ions at* $T = 298.15$ K.

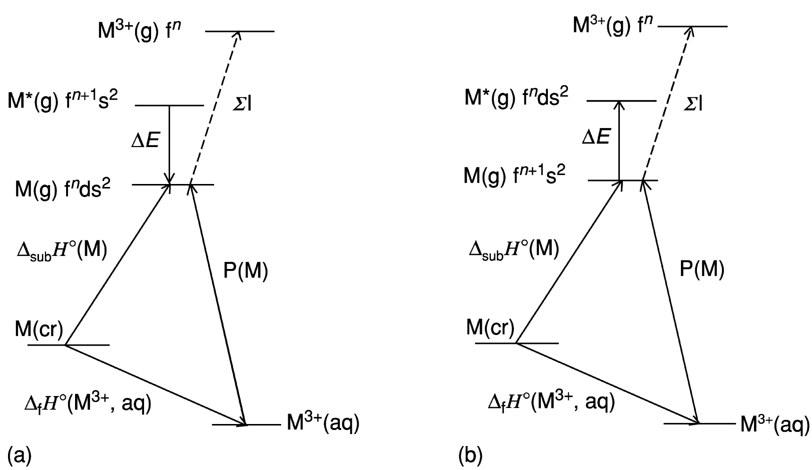

Fig. 19.7 P(M) (*energy level*) *diagrams for trivalent species:* (*a*) *for M = La, Ce, Gd, Lu, Ac–Np, and Cm;* (*b*) *for other lanthanides, and Pu, Am, and Bk–No.*

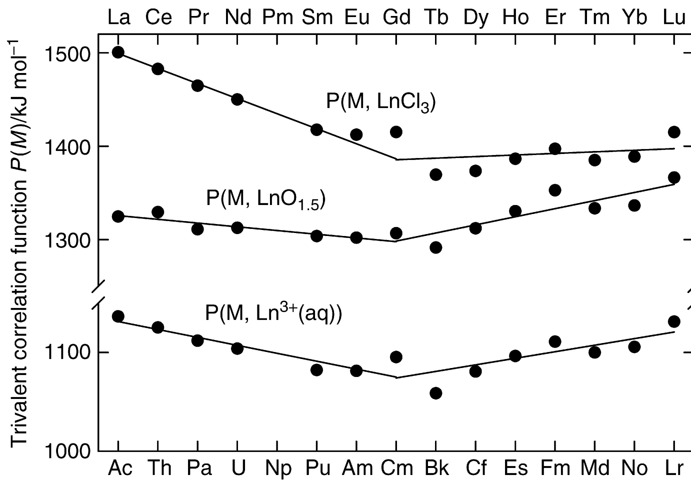

Fig. 19.8 P(M) *function for f-element trichlorides, sesquioxides, and aquo ions.*

refine this $P(M)$ function and to develop similar $P(M)$ plots relating f-block metals and their sesquioxides and trichlorides (Fig. 19.8). David's predictions for $\Delta_f H°(Bk^{3+})$ and $\Delta_f H°(Cf^{3+})$ have been borne out by experiments and consequently, their estimates for the heaviest trivalent actinides are used here. Some enthalpies of formation of tetravalent and higher ions have been calculated from Gibbs energies (electromotive force (EMF) measurements) and entropies (estimates) (Fuger and Oetting, 1976).

Enthalpies of formation of the tetravalent ions Am^{4+} and Cm^{4+} have been estimated from enthalpies of formation and solution of the dioxides (Morss and Fuger, 1981; Morss, 1983, 1985). The enthalpy of formation of Cf^{4+} was obtained from that of Cf^{3+}, the semiempirically deduced standard potential for the Cf^{4+}/Cf^{3+} couple, 3.2 V (see below), and the assumption that the difference in entropies between the Cf^{4+} and the Cf^{3+} ions is the same as for the corresponding Bk system.

19.3.2 Entropies

Entropies of aqueous ions can be determined directly by measuring the enthalpy and Gibbs energy of solution of a salt that contains the ions, and also by measuring the heat capacity of the solid salt and calculating its entropy.

$$\Delta_f S° = (\Delta_f H° - \Delta_f G°)/T \tag{19.3}$$

The absolute entropy of the ion is then calculated from the equation representing $\Delta_f S°$:

$$MX_n(cr) = M^{n+}(aq) + nX^-(aq) \tag{19.4}$$

Standard-state entropies of aqueous ions are by convention referenced to $S°(H^+(aq)) = 0$. Four actinide aqueous-ion entropies (Th^{4+}, Pu^{3+}, UO_2^{2+}, and NpO_2^{2+}) have been determined by the former method.

The temperature coefficient of the EMF of an equilibrium reaction involving the ion can be used to calculate the entropy of the reaction, from which, using auxiliary data, the entropy of formation of the ion can be calculated. This is, for instance, the case of the entropy of the Pu^{4+}(aq) ion. When, for a given reaction, the standard enthalpies of formation of the intervening ions, as well as the standard potential, are known, then the entropy change for this reaction is, of course, fixed. Alternatively, the experimental knowledge of the standard potential and of the entropy change fixes the standard enthalpy of formation.

Fuger and Oetting (1976) summarized all experimental data and selected or estimated entropies of the aqueous ions of Th through Bk. We have adopted their values for the ions of Th, Pa, and Cm. For Bk, we have used the temperature dependence of the Bk $^{4+}$/Bk^{3+} potential by Simakin *et al.* (1977). For the ions of U, Np, Pu, and Am, the values recommended by the NEA-TDB assessment (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003) have been taken. For the aqueous ions beyond Bk, only estimated entropies are available. These estimates are fairly trustworthy because they depend only upon the ionic charges, the ionic radii, and the magnetic degeneracy of the ground states.

Several semiempirical equations have been proposed to fit entropies of aqueous ions to the above parameters, for example (Morss, 1976; Morss and McCue, 1976):

$$S(M^{z+}) = \frac{3}{2}R\ \ln(\text{at.wt.}) + R\ \ln(2J+1) + 256.8 - 32.84(|z|+3)^2/(r+c) \tag{19.5}$$

where $R = 8.314$ J K^{-1} mol^{-1}, J is the total angular momentum quantum number of the ion, z is the ionic charge, r is the ionic radius (in nm) for coordination number 6 taken from Shannon (1976) (except that coordination number 8 is used for $z = 4$), and c is a term added to the radius to represent the inner-sphere hydration: $c = 0.120$ nm for cations and $c = 0.040$ nm for anions. David (1986) has proposed the following equation:

$$S(M^{z+}) = \frac{3}{2}R\ \ln(\text{at. wt.}) + R\ \ln(2J+1) + S_c(r) \tag{19.6}$$

where $S_c(r)$ is a structural entropy term, dependent for a given z only on the hydrated-ion structure. Equation (19.6) was devised by David to take into account the change in inner-sphere hydration number from 9 to 8 between Sm and Tb in the Ln^{3+} ions and between Cm and Es in the An^{3+} ions. Very recently, David and coworkers (David and Vokhmin, 2001, 2002; David *et al.*, 2001) developed a hydration and entropy model for covalent and ionic ions, leading to estimates very close to those obtained earlier. We thus accept David's estimates of the heavy An^{3+} ion entropies. Equation (19.5) has been used for divalent and tetravalent ions (Table 19.3). The necessary ionic radii for equation (19.5) were estimated by comparison of isoelectronic 4f and 5f ions as well as by Shannon-type plots of unit-cell volumes of dihalides and dioxides against r^3. Other predictive equations give fairly consistent entropy estimates (Lebedev, 1981; David, 1986) even though ionic radii as small as 100 pm for No^{2+} have been estimated (Silva *et al.*, 1974; David, 1986).

For the An^{4+} ions the situation is less clear. Entropy values have been derived for Th^{4+}, U^{4+}, Np^{4+}, and Pu^{4+} from experiments. However, the trend in the values for these compounds, even when corrected for the $R\ln(2J+1)$ contribution, is not smooth as one could expect from equation (19.6), as shown by Konings (2001a), who suggested that the Np^{4+} value may be in error. He suggested $S°(Np^{4+}$, aq, 298.15 K) $= -414$ J K^{-1} mol^{-1}, which is the lower limit of the experimental value, $-(426.4 \pm 12.4)$ J K^{-1} mol^{-1} as given by NEA (Lemire *et al.*, 2001). Also his estimate for Am^{4+} (-422 J K^{-1} mol^{-1}) is different from the NEA value $-(406 \pm 21)$ J K^{-1} mol^{-1} (Silva *et al.*, 1995). Clearly further experiments are needed to resolve these discrepancies.

19.3.3 Electrode potentials

Fuger and Oetting (1976) assessed the reversible cell EMF and polarographic data that allowed them to calculate Gibbs energy differences between many aqueous-ion pairs. By this way they were able to connect all aqueous ions and to tabulate Gibbs energies of formation of all actinide aqueous ions in acid solution. Comprehensive summaries of reduction potential literature values have been assembled by Martinot (1978) and Martinot and Fuger (1985). The latter authors have presented reduction potentials in acid solution for all of these elements including estimates of the reduction potentials for the Bk^{3+}/Bk and Cf^{3+}/Cf couples, based on calorimetric measurements on Bk^{3+}(aq) and Cf^{3+}(aq) (Fuger *et al.*, 1981, 1984). The reduction potentials of the U, Np, Pu, and Am ions were discussed extensively and assessed in the NEA-TDB series (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

No selection was made by Fuger and Oetting (1976) and by Lemire *et al.* (2001) for the heptavalent/hexavalent neptunium and plutonium couples, although the literature values were discussed. We adopt here, for the formal potentials in 1 mol dm^{-3} NaOH the values (0.59 ± 0.05) V and (0.85 ± 0.05) V for the Np(VII/VI) and Pu(VII/VI) couples, respectively, from the review of Perethrukhin *et al.* (1995). Conventionally, we write the heptavalent species as MO_3^+, noting that, in neptunium, strong arguments have been brought recently in support of the existence of the tetroxo species $NpO_4(OH)_2^{3-}$ in 1 mol dm^{-3} NaOH (Williams *et al.*, 2001). Reduction of Np(VII) to NpO_2^{2+} in acid media occurs rapidly: we will take for the 1 mol dm^{-3} $HClO_4$ medium,

Table 19.3 *Thermodynamic properties of the actinide aqueous ions, see text for references; estimated values in italics.*

	An^{3+}		An^{4+}		AnO_2^{+}		AnO_2^{2+}		
	S°(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$(298.15 K) (kJ mol^{-1})	S° (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$(298.15 K) (kJ mol^{-1})	S°(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$(298.15 K) (kJ mol^{-1})	S°(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$(298.15 K) (kJ mol^{-1})	*References*
Ac	*–180 ± 17*	*–653 ± 25*							a
Th			–422.6 ± 16.7	–769.0 ± 2.5					a
Pa			*–397 ± 40*	–621.4 ±14.3[b,c]	*–21 ± 21*	–1115 ± 21[c,d]			b
U	–188.2 ± 13.9	–489.1 ± 3.7	–416.9 ± 12.6	–591.2 ±3.3	–25 ± 8	–1025.1 ± 3.0	–98.2 ± 3.0	–1019.0 ± 1.5	e
Np	–193.6 ± 20.3	–527.2 ± 2.1	–426.4 ± 12.4	–556.0 ± 4.2	–45.9 ± 10.7	–978.2 ± 4.6	–92.4 ± 10.5	–860.7 ± 4.7	e
Pu	–184.5 ± 6.2	–591.8 ± 2.0	–414.5 ± 10.2	–539.9 ± 3.1	1 ± 30	–910.1 ± 8.9	–71.2 ± 22.1	–822.0 ± 6.6	e
Am[i]	–201 ± 15	–616.7 ± 1.5	–406 ± 6	–406 ± 21	–21 ± 10	–804.3 ± 5.4	–88 ± 10	–650.8 ± 4.8	e
Cm	–191 ± 10	–615.0 ± 6.0	–439 ± 15	–380 ± 10					f
Bk	*–194 ± 17*	–601 ± 5	–402 ± 17	–483 ± 5					g
Cf	*–197 ± 17*	–577 ± 5	*–405 ± 17*	*311 ± 13*					h
Es	*–206 ± 17*	*–603 ± 21*							h
Fm	*–215 ± 25*	*–632 ± 42*							h
Md	*–224 ± 25*	*–538 ± 42*							h
No	*–231 ± 25*	*–395 ± 42*							h
Lr	*–255 ± 25*	*–630 ± 42*							h

[a] Fuger and Oetting (1976).
[b] Recalculated by the present authors from Fuger *et al*. (1983).
[c] In 1 mol dm^{-3} HCl.
[d] For the species $PaOOH^{2+}$.
[e] NEA-TDB (Grenthe *et al*., 1992; Silva *et al*., 1995; Lemire *et al*., 2001; Guillaumont *et al*., 2003).
[f] Konings (2001a).
[g] See text.
[h] Estimated.
[i] S° (Am^{2+}, aq, 298.15 K) = –(1 ± 15) J K^{-1} mol^{-1} and $\Delta_f H^\circ$ (Am^{2+}, aq, 298.15 K) = –(355 ± 16) kJ mol^{-1}.

the value (2.04 ± 0.05) V from the determination of Musikas *et al.* (1974). For the corresponding Pu and Am couples in the same medium, Perethrukhin suggested the values (2.3 ± 0.1) V and (2.5 ± 0.1) V, respectively. The uncertainties have been increased, compared to those given in the references cited. No value exists for the corresponding Pu couple in acid media, which is even more oxidizing. The question of the existence of any Am(VII), even in basic media, has been briefly discussed by Silva *et al.* (1995), and no selection was made.

The heavier actinide ions present especially challenging problems. These elements have short-lived isotopes with available amounts ranging between micrograms and single atoms. They also have accessible divalent states. To achieve meaningful experimental measurements on these ions, Maly (1967) and Maly and coworkers (Maly and Cunningham, 1967; Maly *et al.*, 1968), as well as Samhoun and David (1976) and David (1986) developed radioelectrochemical tracer methods, and Mikheev (1983) and his coworkers developed co-crystallization systematics. Judicious application of radiopolarography, radiocoulometry, amalgamation energies, and co-crystallization has yielded $E°$ for An^{3+}/An^{2+}, An^{2+}/An, and An^{3+}/An couples (David, 1986) and has provided Gibbs energies of formation for Es^{3+}, Md^{3+}, and No^{3+}. The best Gibbs energies of formation of Fm^{3+} and Lr^{3+} have actually been calculated from estimates of enthalpies of sublimation, promotion energies $P(M)$, and entropies (David, 1986). Fig. 19.9 summarizes standard reduction potentials that are consistent with the Gibbs energies of formation calculated from enthalpies of formation and standard entropies. Because of the necessity of making EMF measurements in strongly acidic solution, and the impossibility of making measurements approaching standard state (nearly neutral solution), both the Gibbs energies of formation and reduction potentials refer to formal potentials rather than standard potentials (unit concentration rather than unit activity of hydrogen ion). When no thermochemical data were available, notably for the divalent ions, the potentials have been estimated.

The reduction potentials in Fig. 19.9 are 'Latimer' diagrams showing the potentials of half-reactions in which the left-hand species is reduced to the right-hand species with the appropriate number of electrons, H^+, and H_2O to balance the half-reaction. (Species not found in aqueous solution, but whose thermodynamic properties have been estimated, are indicated in parentheses.)

The potentials are summarized in Fig. 19.10 as $nE°$, a property proportional to $\Delta_f G°$, versus n, the oxidation state, so that the lowest-lying species for each element is the one most stable in equilibrium with the H^+/H_2 couple.

A substantial number of studies have dealt with the electrochemical behavior of complexed actinides in aqueous solution. Complexation of f-block ions by ligands such as carbonate and polyphosphotungstate has allowed otherwise unstable species such as Am(IV) and U(V) to be studied electrochemically (Kosyakov *et al.*, 1977; Volkov *et al.*, 1981; Hobart *et al.*, 1982, 1983). Carbonate and bicarbonate stabilize acidic cations at relatively high pH (typical

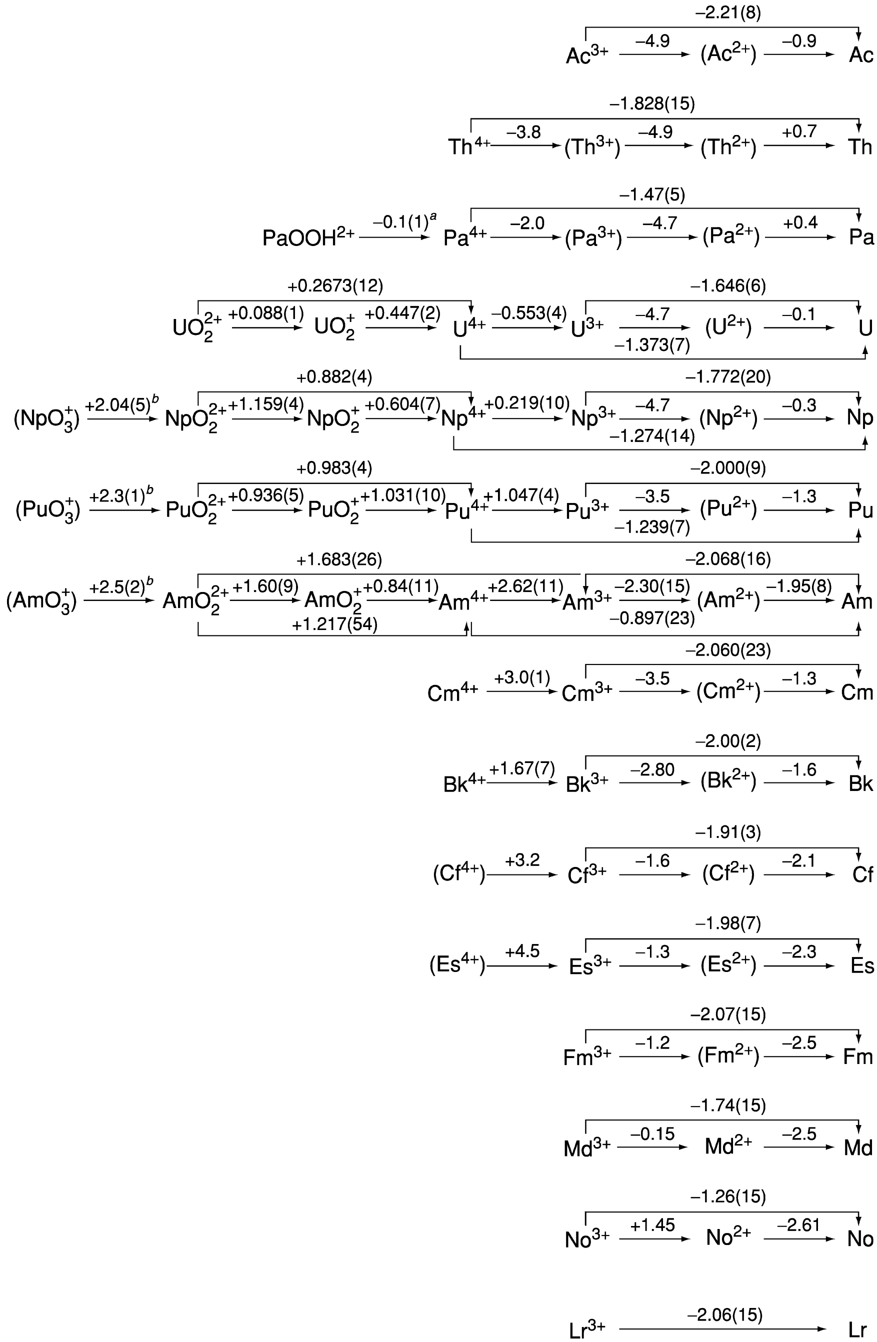

Fig. 19.9 *Standard reduction potentials diagrams for the actinide ions (values in volts versus standard hydrogen electrode);* [a] *indicates that the solvent is* 1 mol dm^3 *HCl,* [b] *refers to the potentials in* 1 mol dm^3 $HClO_4$.

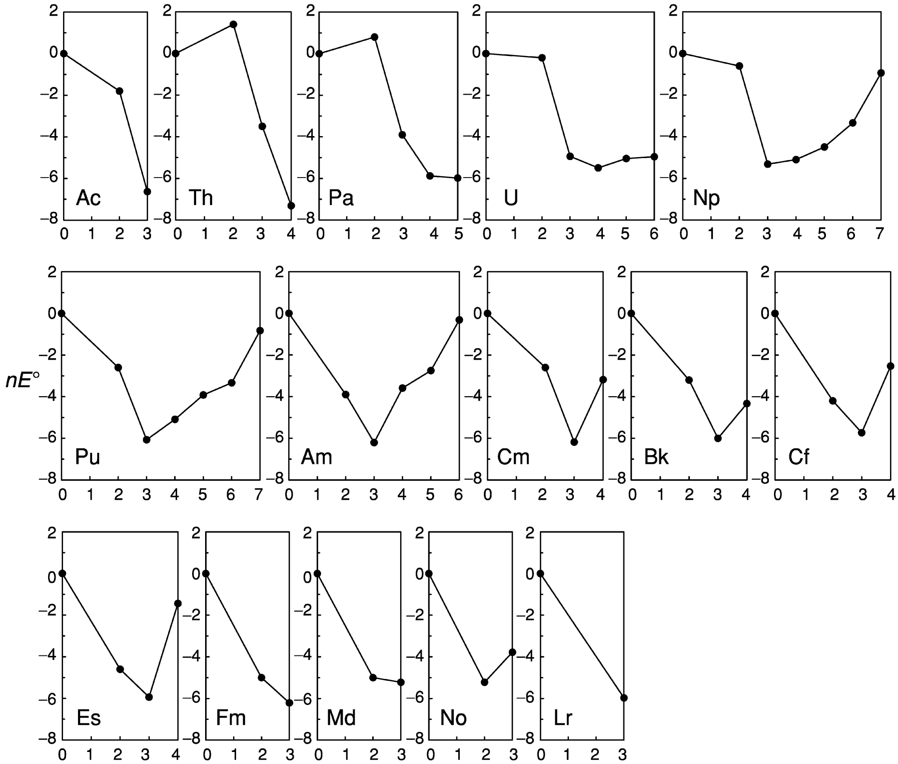

Fig. 19.10 *Comparative stability of actinide aqueous ions (relative to the $H^+(aq)/H_2(g)$ couple).*

of environmental and biological systems), and many actinide–carbonate studies have been reviewed (Cleveland, 1979; Newton and Sullivan, 1985).

Ions that are stabilized as complexes can be utilized to determine standard redox potentials. The $E°(Am^{4+}/Am^{3+})$ measured by cyclic voltammetry in 2 M $Na_2CO_3/NaHCO_3$ at pH 9.7, namely (0.92 ± 0.01) V, could be corrected for the preferred complexation of Am(IV) in this medium by 1.7 V to yield $E°(Am^{4+}/Am^{3+})$ = (2.6 ± 0.1) V (Hobart *et al.*, 1982), in good agreement with the accepted (Fig. 19.2) thermochemical value of (2.62 ± 0.09) V.

Polyphosphotungstate appears to be able to complex Cm(IV) and Cf(IV) sufficiently well to stabilize these ions in aqueous solution (Kosyakov *et al.*, 1977). Because the An^{4+}/An^{3+} potential shift of 1.7 V in carbonate is more favorable for stabilization of An^{4+} than is the shift of 1.0 V in polyphosphotungstate (Volkov *et al.*, 1981), it was expected that Cm(IV) and Cf(IV) would be readily produced in carbonate. Such was not found to be the case, however (Hobart *et al.*, 1983).

19.3.4 Heat capacities

Heat capacities, as well as entropies, of aqueous ions are the fundamental thermodynamic properties that reflect their structure and hydration. Heat capacities are also necessary for the calculation of other thermodynamic properties at temperatures other than 298.15 K. For the actinides, high-temperature properties (at least to 473 K) are essential for calculation of redox, complexation, and heterogeneous equilibria, which are useful in separation and waste management technologies.

The most thorough treatment of uranium and plutonium aqueous-ion equilibria over extended temperatures is that of Lemire and Tremaine (1980). This paper uses the systematic relationships developed by Criss and Cobble (1964), which relate aqueous-ion entropies, heat capacities, and their high-temperature behavior. Lemire and Tremaine had to rely on estimated heat capacities for almost all of their calculations, and most of their equilibrium constants are uncertain by two or more orders of magnitude. Lemire (1984) has also written a report on neptunium aqueous-ion equilibria over extended temperatures. However, in more recent years, the limitations of the Criss–Cobble relationships, when applied to tri- and quadrivalent aqueous species became more apparent. For instance, Shock *et al.* (1997), using the revised Helgerson–Kirkham–Flowers equation of state for aqueous ions, estimated $C^{\circ}_{p,m}(U^{3+}, \text{aq}, 298.15\ \text{K}) = -125.3\ \text{J K}^{-1}\ \text{mol}^{-1}$, distinctly more negative than the value $-(64 \pm 22)\ \text{J K}^{-1}\ \text{mol}^{-1}$ (mean value over the temperature range 298–473 K) accepted by Grenthe *et al.* (1992) from the estimate reported by Lemire and Tremaine. For another trivalent ion, Al^{3+}, Hovey and Tremaine (1986) have determined $C^{\circ}_{p,m}(Al^{3+}, \text{aq}, 298.15\ \text{K}) = -119\ \text{J K}^{-1}\ \text{mol}^{-1}$, whereas the Criss–Cobble relationship leads to $16\ \text{J K}^{-1}\ \text{mol}^{-1}$.

For quadrivalent actinide ions, the Criss–Cobble relation leads to −28, −48, and $-63\ \text{J K}^{-1}\ \text{mol}^{-1}$ for Th^{4+} (Morss and McCue, 1976), U^{4+}, and Pu^{4+} (Lemire and Tremaine, 1980), respectively. However, Hovey (1997) has determined recently $C^{\circ}_{p,m}(Th^{4+}, \text{aq}, 298.15\ \text{K}) = -(224 \pm 5)\ \text{J K}^{-1}\ \text{mol}^{-1}$. The flow microcalorimetric technique used by this author, under conditions minimizing hydrolysis and complexation, is far superior to measurements of integral heats of dilution or solution used in two previous studies (Apelblatt and Sahar, 1975; Morss and McCue, 1976). From the above, it appears that the Criss–Cobble relationships underestimate the heat capacities of tri- and quadrivalent ions by 100–160 $\text{J K}^{-1}\ \text{mol}^{-1}$. The values adopted recently by the NEA-TDB assessment (Guillaumont *et al.*, 2003) $C^{\circ}_{p,m}(U^{3+}, \text{aq}, 298.15\ \text{K}) = -(150 \pm 50)\ \text{J K}^{-1}\ \text{mol}^{-1}$ and $C^{0}_{p,m}(U^{4+}, \text{aq}, 298.15\text{K}) = -(220 \pm 50)\text{J K}^{-1}\ \text{mol}^{-1}$ are in line with $C^{\circ}_{p,m}(Th^{4+}, \text{aq}, 298.15\ \text{K}) = -(224 \pm 5)\ \text{J K}^{-1}\ \text{mol}^{-1}$ (Hovey, 1997).

The value $C^{\circ}_{p,m}(UO_2^{2+}, \text{aq}, 298.15\,\text{K}) = (42.4 \pm 3.0)\ \text{J K}^{-1}\text{mol}^{-1}$, and the function $C^{\circ}_{p,m}(UO_2^{2+}, \text{aq}, T) = \{350.5 - 0.8722(T/K) - 5308((T/K) - 190)^{-1})\}$

$\mathrm{J\,K^{-1}mol^{-1}}$, for the temperature range 283–328 K, adopted in the NEA assessment (Grenthe *et al.*, 1992) is also based on sound experiments (Hovey *et al.*, 1989).

For actinide ions, with 1+ charge, the only experimental results $C^{\circ}_{\mathrm{p,m}}(\mathrm{NpO_2^+}, \mathrm{aq}, 298.15\ \mathrm{K}) = -(4 \pm 25)\ \mathrm{J\,K^{-1}\,mol^{-1}}$, and $C^{\circ}_{\mathrm{p,m}}(\mathrm{NpO_2ClO_4}, \mathrm{aq}, T) = \{3.56779 \times 10^3 - 4.95931(T/K) - 6.32244 \times 10^5 (T/K)^{-1}\}\ \mathrm{J\,K^{-1}\,mol^{-1}}$ in the temperature range 291–373 K, adopted in the NEA assessment (Lemire *et al.*, 2001) depend on measurements by Lemire and coworkers (Lemire *et al.*, 1993; Lemire and Campbell, 1996a) on $\mathrm{NpO_2ClO_4}$ solutions. Use of $C^{\circ}_{\mathrm{p,m}}(\mathrm{HClO_4}, \mathrm{aq}, T) = \{3.25118 \times 10^3 - 4.86333(T/K) - 5.45295 \times 10^5 (T/K)^{-1}\}\ \mathrm{J\,K^{-1}\,mol^{-1}}$, in the same temperature range, from Lemire and Campbell (1996b) leads to $C^{\circ}_{\mathrm{p,m}}(\mathrm{NpO_2^+}, \mathrm{aq}, T) = \{0.31661 \times 10^3 - 0.09598(T/K) - 0.87049 \times 10^5 (T/K)^{-1}\}$ $\mathrm{J\,K^{-1}\,mol^{-1}}$, with $C^{\circ}_{\mathrm{p,m}}(\mathrm{H^+}, \mathrm{aq}, T) = 0\ \mathrm{J\,K^{-1}\,mol^{-1}}$ in the reported temperature range.

Obviously, in recent years, progress has been made in our knowledge of the behavior of the electrolytes at high temperature. Nevertheless, more heat capacity data are needed for the multicharged ions.

19.4 IONS IN MOLTEN SALTS

Electrochemistry of actinides in molten salts has been pursued by many authors. The main incentives have been the molten salt reactor development and the pyrochemical reprocessing of spent fuel. The early work (up to 1980) has been summarized through reviews (Gruen, 1976; Plambeck, 1976; Martinot, 1978, 1982). In some cases, such as hydroxide and carbonate melts, high oxidation states of the actinides are stabilized, whereas in halide melts the use of strong Lewis acid molten salts stabilizes lower oxidation states (4+, 3+, and 2+). Coprecipitation of lanthanide tri- and dichlorides and oxychlorides with trace amounts of some actinides has yielded some $\mathrm{An^{3+}/An^{2+}}$ E° values and has produced evidence (unconfirmed by other methods) of divalent Pu, Cm, and Bk (Mikheev, 1983).

We will briefly summarize the data for the fluoride ($\mathrm{LiF{-}BeF_2}$) and chloride (LiCl–KCl) systems as these are of interest to the renewed studies of the molten salt reactor and the pyrochemical reprocessing of spent fuel, in the framework of the partitioning and transmutation (P&T) and advanced nuclear reactor development programs worldwide. The apparent standard potentials are summarized in Tables 19.4 and 19.5.

The data for the actinide fluorides in $\mathrm{LiF{-}BeF_2}$ (0.67:0.33 molar ratio) are taken from the review of Martinot (1982) who selected the data assessed by Baes (1966, 1969) for the Molten Salt Reactor Experiment (MSRE). These data are not based on electrochemical measurements but are derived from chemical

Table 19.4 *Apparent standard potentials in molten LiF–BeF$_2$* (0.67:0.33 molar ratio) *calculated versus the HF(g)* + e^- = F^- + $H_2(g)$ *reference system* [*after Baes* (1966, 1969)].

	E^0 (V)	T (K)	$\Delta_f S°$ (J K^{-1} mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})
Th^{4+}/Th^0	$-2.498 + 0.720\ 10^{-3}(T/K)$	700–1000	–277.9	–964.1
U^{3+}/U^0	$-2.059 + 0.626\ 10^{-3}(T/K)$	700–1000	–181.2	–596.0
U^{4+}/U^0	$-2.007 + 0.671\ 10^{-3}(T/K)$	700–1000	–259.0	–774.6
Pu^{3+}/Pu^0	$-2.313 + 0.788\ 10^{-3}(T/K)$	700–1000	–228.1	–669.5

Table 19.5 *Apparent standard potentials in molten LiCl–KCl* (*eutectic*) *calculated versus the* Cl_2/Cl^- *reference system; estimated values are in italics.*

	E^0 (V)	T (K)	$\Delta_f S°$ (J K^{-1} mol^{-1})	$\Delta_f H°$ (kJ mol^{-1})	*References*
Th^{4+}/Th^0	$-2.86 + 0.50 \times 10^{-3}(T/K)$	673–773			a,b
Pa^{4+}/Pa^0	$-2.754 + 0.60 \times 10^{-3}(T/K)$	673–773	–231.6	–1062.9	b
U^{3+}/U^0	$-2.962 + 0.6115 \times 10^{-3}(T/K)$	673–773	–177.0	–857.4	b
U^{4+}/U^0	$-2.677 + 0.5726 \times 10^{-3}(T/K)$	673–773	–221.0	–1033.2	b
Np^{3+}/Np^0	$-3.119 + 7.45 \times 10^{-4}(T/K)$	673–773	–231.6	–902.9	c
Pu^{3+}/Pu^0	$-3.319 + 7.45 \times 10^{-4}(T/\mathrm{K})$	673–773	–203.9	–960.6	c
Am^{2+}/Am^0	$-3.259 + 5.50 \times 10^{-4}(T/K)$	673–773	–106.1	–628.8	d
Am^{3+}/Am^0	$-3.55 + 1.0 \times 10^{-3}(T/K)$	723–773	–289.5	–1028.4	d
Cm^{3+}/Cm^0	*–2.83*	723	–	–	e

[a] Plambeck (1976).
[b] Martinot (1982).
[c] Roy *et al.* (1996).
[d] Fusselman *et al.* (1999).
[e] Estimated in this work.

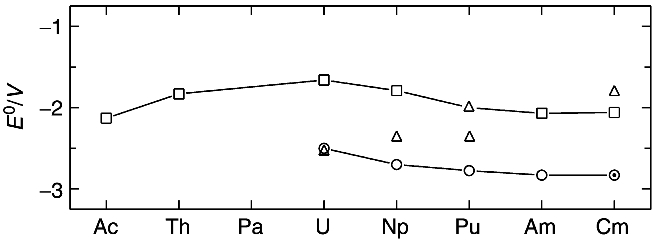

Fig. 19.11 *The electrode potentials of An^{3+}/An^0 couples in aqueous solution* (□) *and in LiCl–KCl eutectic at* 773 K (○)*; the results of Martinot* (1982) *are also shown* (Δ) *for information* (*see text*)*; estimated values are indicated by* (⊙).

equilibria in LiF–BeF_2 (0.67:0.33). For example, the uranium potentials were derived from the equilibria:

$$UO_2(s) = U^{4+}(sln) + 2\,O^{2-}(sln) \tag{19.7}$$

$$\frac{1}{2}\,H_2(g) + UF_4(sln) = UF_3(sln) + HF(g) \tag{19.8}$$

via the Gibbs energies of formation, scaling the results to the HF/F^- and the Be^{2+}/Be^0 couples.

Martinot (1982) summarized the data for the actinides in molten chloride salts, primarily based on his own electrochemical measurements. But recently many new studies have been reported on plutonium and americium in LiCl–KCl (Roy *et al.*, 1996; Fusselman *et al.*, 1999; Lambertin *et al.*, 2000; Serp *et al.*, 2004). Here a contradictory observation is made: the results of Martinot indicate an increase of the apparent potential of the An^{3+}/An^0 couple from U to Cm, whereas the more recent results indicate the opposite trend (Fig. 19.11), which is in agreement with the trend in potentials of the aqueous ions. Baes (1966) indeed noted that the potentials in molten salts correlate very well with those in solutions, and for that reason we reject the results of Martinot. Recently, data on Am^{2+}/Am^0 couple have been obtained (Fusselman *et al.*, 1999). Yamana and Moriyama (2002) measured the Ln^{2+}/Ln^{3+} couples of Nd, Eu, Dy, and Yb and showed an excellent correlation with the aqueous Ln^{2+}/Ln^{3+} potentials.

19.5 OXIDES AND COMPLEX OXIDES

19.5.1 Binary oxides with O/An > 2.00

Many binary uranium oxides with O/U > 2.00 are known, and the thermodynamic properties of most of them are well established (see Table 19.6). The room temperature values for γ-UO_3 and U_3O_8 are CODATA Key Values (Cox *et al.*, 1989); those of the other binary uranium compounds have been reviewed

Table 19.6 *Thermodynamic properties of the crystalline binary actinide oxides with O/An >2.00; estimated values in italics.*

	C_p(298.15 K) (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
γ-UO_3	81.67 ± 0.16	96.11 ± 0.40	–1223.8 ± 1.2	a,b
β-UO_3	81.34 ± 0.16	96.32 ± 0.40	–1220.3 ± 1.3	a
α-UO_3	81.84 ± 0.30	99.4 ± 1.0	–1212.41 ± 1.45	a
δ-UO_3			–1213.73 ± 1.44	a
ε-UO_3			–1217.2 ± 1.3	a
am-UO_3			–1207.9 ± 1.4	a
α-$UO_{2.95}$			–1211.28 ± 1.28	a
U_3O_8	237.93 ± 0.48	282.55 ± 0.50	–3574.8 ± 2.5	a
α-U_3O_7	214.26 ± 0.90	246.51 ± 1.50		a
β-U_3O_7	215.52 ± 0.42	250.53 ± 0.60	–3423.0 ± 6.0	a
U_4O_9	293.36 ± 0.45	334.12 ± 0.68	–4512.0 ± 6.8	a
NpO_3	–	*100 ± 10*	*–1070 ± 6*	c
Np_2O_5	–	*174 ± 20*	–2162.7 ± 9.5	a,c

[a] NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[b] Cox *et al.* (1989).
[c] Morss and Fuger (1981).

by Grenthe *et al.* (1992). Pa_2O_5 and Np_2O_5 are the only other well-known binary oxide with O/An > 2.00. None of the thermodynamic properties of Pa_2O_5 have been measured. Those of Np_2O_5 are fairly well established through enthalpy of formation measurements (Belyaev *et al.*, 1979; Merli and Fuger, 1994) and high-temperature enthalpy increment measurements (Belyaev *et al.*, 1979) that have been reviewed by Lemire *et al.* (2001). Because of the better stoichiometry and better thermochemical cycle used by Merli and Fuger, the $\Delta_f H°(Np_2O_5,cr)$ derived from that work has been accepted. No lanthanide comparison for these compounds can be made because there are no lanthanide oxides with O/Ln > 2.00. Recently the existence of PuO_{2+x} with x up to 0.5 has been claimed (Haschke *et al.*, 2001) and its thermodynamic properties have been estimated (Haschke and Allen, 2002).

19.5.2 Dioxides

(a) Enthalpy of formation

The dioxides from ThO_2 through CfO_2 are all known, but many of these have not been studied thermodynamically (see Table 19.7). Because the enthalpy of formation values of ThO_2, UO_2 (CODATA Key Values, see Cox *et al.*, 1989) and NpO_2 to CmO_2 are based on a sound experimental basis, the values for the other actinide dioxides can be estimated with reasonable accuracy.

Table 19.7 *Thermodynamic properties of the crystalline actinide dioxides at* 298.15 K*; estimated values are in italics.*

	S_{exs} (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
ThO_2	0	65.23 ± 0.20	–1226.4 ± 3.5	a
PaO_2	*14.90*	*80 ± 5*	*–1107 ± 15*	b
UO_2	9.34	77.03 ± 0.20	–1085.0 ± 1.0	a
NpO_2	14.15	80.30 ± 0.40	–1074.0 ± 2.5	c
PuO_2	1.55	66.13 ± 0.26	–1055.8 ± 1.0	c
AmO_2	12.46	*78 ± 5*	–932.3 ± 2.5	c,d
CmO_2	0.00	*65 ± 5*	–912.1 ± 6.8	d
BkO_2	*17.29*	*83 ± 5*	*–1023 ± 9*	b
CfO_2	*21.3*	*87 ± 5*	*–857 ± 14*	b

[a] Cox *et al.* (1989).
[b] Estimated in the present work.
[c] NEA-TDB (Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[d] Konings (2001b).

Morss and Fuger (1981) established that the reaction enthalpy of the idealized dissolution reaction

$$AnO_2(c) + 4H^+(aq) \rightarrow An^{4+}(aq) + 2H_2O(l) \tag{19.9}$$

varies regularly in the actinide series. The enthalpy of this reaction represents in part the difference between the lattice enthalpy of the crystalline dioxide and the enthalpy of hydration of its ionic components. Both these properties are difficult to calculate and change substantially as a function of ionic properties, whereas their difference (the enthalpy of solution) should change slowly and smoothly as a function of ionic size. Because the enthalpies of formation of H^+(aq) and H_2O(l) are constant in this equation, the quantity $\{\Delta_f H°(MO_2, cr) - \Delta_f H°(M^{4+}, aq)\}$ can be used for establishing relationships. Fig. 19.12 shows the relation with the molar volume of the unit cell. Ionic radii could have been used, because these are tabulated as a function of coordination number, but often they are reliable to only two significant figures. The values for PaO_2, BkO_2, and CfO_2 can be derived by interpolation or extrapolation of the linear relationship. These values are included in Table 19.7.

(b) Entropy

The low-temperature heat capacities have been measured for the solid dioxides from ThO_2 to PuO_2 and standard entropies for these compounds are known (see Table 19.7). The values for ThO_2 and UO_2 are CODATA Key Values (Cox *et al.*, 1989), those for NpO_2 and PuO_2 have been evaluated by the NEA-TDB (Lemire *et al.*, 2001). Konings (2001a) estimated the entropies of AmO_2 and CmO_2, proposing that the $S°$(298.15 K) of these compounds can be adequately

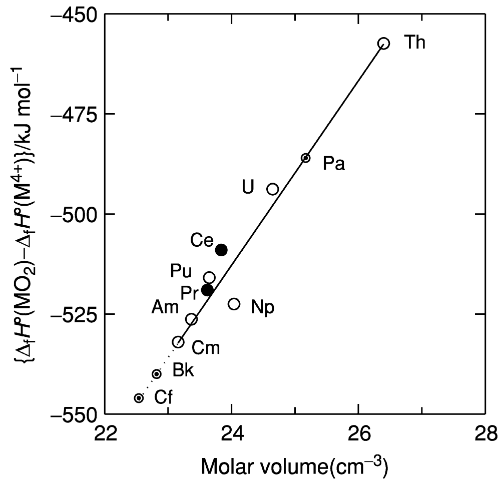

Fig. 19.12 *The difference between the enthalpies of formation of f-element dioxides and the corresponding M^{4+} aqueous ions; lanthanides* (•), *actinides* (○), *and estimated values* (⊙).

described as the sum of a lattice component and an excess component arising from f-electron excitation:

$$S = S_{\text{lat}} + S_{\text{exs}} \tag{19.10}$$

S_{lat} was assumed to be the value for ThO_2 and S_{exs} was calculated from the crystal field energies of these compounds (Krupa and Gajek, 1991; Krupa, 2001). Good agreement with the experimental values for UO_2, NpO_2, and PuO_2 was found and the description explains the significantly lower entropy value of PuO_2 among these compounds. This estimation procedure was adopted in the recent evaluation of the entropies of Am compounds by the NEA-TDB project (Guillaumont *et al.*, 2003). In a subsequent study, Konings (2004a) argued that the experimental data give evidence that S_{exs} is composed of two terms, the f-electron excitation and a residual term:

$$S_{\text{exs}} = S_{\text{f}} + S_{\text{res}} \tag{19.11}$$

We have used a similar method to estimate the entropies of PaO_2, BkO_2, CfO_2, and EsO_2, where in absence of crystal field data, the excess contribution was calculated from the degeneracy of the unsplit ground state, which probably overestimates the entropy somewhat.

(c) High-temperature properties

The high-temperature properties of the major actinide dioxides (UO_2, ThO_2, PuO_2) have been reviewed by many authors. The data are mostly restricted to the solid phase, except for UO_2, which has been studied in detail in the crystal, liquid, and gas phases (up to 8000 K) for obvious reasons. Fink (2000) reviewed the thermophysical properties of UO_2 recently and presented recommended values for a large number of thermodynamic and thermophysical properties. Numerous equations of state for UO_2 have been published, the most recent and complete one by Ronchi *et al.* (2002). Also the high-temperature properties of thorium oxide in the crystal phase are reasonably well established (Bakker *et al.*, 1997). The melting points of the actinide dioxides are shown in Fig. 19.13 along with those for the lanthanide and actinide sesquioxides.

The high-temperature heat capacities of ThO_2, UO_2, and PuO_2 are shown in Fig. 19.14. The heat capacity approaches the Dulong–Petit value ($9R = 74.8$ J K^{-1} mol^{-1}) between 500 and 1500 K. In this temperature range the lattice contributions dominate the heat capacity with a minor but significant

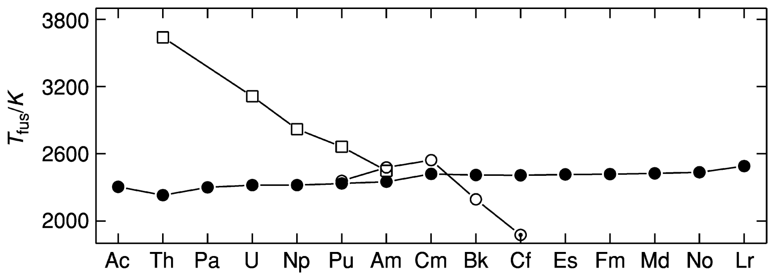

Fig. 19.13 *The melting points of the lanthanide sesquioxides* (•), *the actinide sesquioxides* (○) *and actinide dioxides* (□); *estimated values are indicated by* (⊙).

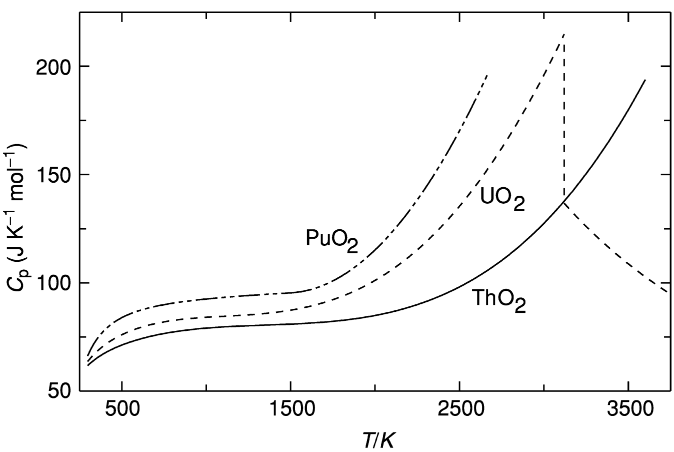

Fig. 19.14 *The high-temperature heat capacity of the actinide dioxides* (*see Table* 19.9).

contribution of 5f electron excitations. Peng and Grimvall (1994) showed that for ThO_2 and UO_2 the harmonic lattice contributions dominate up to about 500 K; above that temperature, the anharmonic contributions should be included.

As discussed in Section 19.5.2(b), the difference between the heat capacity of ThO_2 and the other actinide dioxides in the temperature range up to 1500 K is mainly due to the excess contribution arising from the population of excited f-electron levels of the An^{4+} ions:

$$C_p = C_{lat} + C_{exs} \tag{19.12}$$

Thus the heat capacity of the other actinide dioxides can be approximated by adding C_{exs}, which can be calculated from electronic energy levels.

Above 1500 K, the heat capacity strongly increases towards the melting point. In this temperature range, λ-type phase transitions have been observed for UO_2 (Hiernaut *et al.*, 1993) as well as ThO_2 (Ronchi and Hiernaut, 1996) at about $0.85T_{fus}$, which are related to order–disorder anion displacements in the oxygen sublattice. Below the phase transition, the formation of Frenkel lattice defects is the main cause of the rapid increase of the heat capacity; above the phase transition, Schottky defects become more important. The experimental data for PuO_2 by Ogard (1970) suggest a similar effect above 2400 K, but it has been attributed to partial melting of PuO_2 through interaction with the tungsten container (Fink, 1982; Oetting and Bixby, 1982). Because no clear evidence exists for this interaction, it has been included in the recommended equations given in this work (unlike in Cordfunke and Konings, 1990; Lemire *et al.*, 2001).

The experimental heat capacity data for NpO_2 (Arkhipov *et al.*, 1974) are in poor agreement with the low-temperature data and with the values estimated by Yamashita *et al.* (1997) and Serizawa *et al.* (2001). These authors calculated the lattice heat capacity from the phonon and dilatation contributions using Debye temperature, thermal expansion, and Grüneisen constants, and the electronic contributions from crystal field energies. No experimental data are known for PaO_2 and AmO_2. CmO_2 is unstable above 653 K.

As shown in Fig. 19.13 the melting points of the dioxides steadily decrease from ThO_2 to PuO_2, the change being more than 1200 K. This strong variation is accompanied by a strong increase in the oxygen pressure as the dioxides start to lose oxygen according to the reaction

$$MO_2(c) = MO_{2-x}(s) + \frac{x}{2}O_2(g) \tag{19.13}$$

which for PuO_2 and AmO_2 is already significant below the melting point, which means that the melting points are only defined in an oxygen atmosphere. The decrease of stability is related to the strong changes in stability of the 4+ oxidation states. Only the melting enthalpy of UO_2 is known with some accuracy. The values for the other dioxides have been estimated assuming that the entropy of melting is constant along the AnO_2 series.

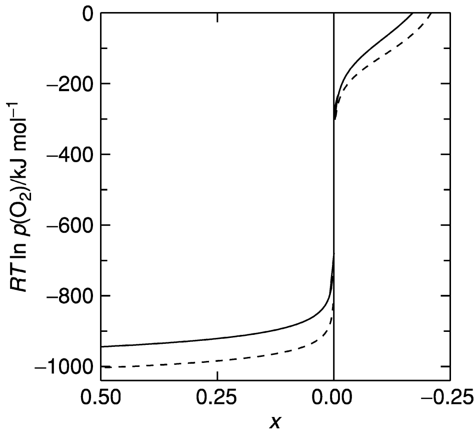

Fig. 19.15 *The oxygen potential of* UO_{2-x} *at* 1500 K (*solid line*) *and* 1250 K (*broken line*) *as a function of x calculated from the Lindemer and Besmann* (1985) *model; note that the hyperstoichiometric range is given with negative values.*

Recommended equations for the high-temperature heat capacity are given in Table 19.8.

(d) Nonstoichiometry

The actinide dioxides are well known for their wide ranges of nonstoichiometry. Hypostoichiometry has been reported for all actinide dioxides. Hyperstoichiometry is only known for UO_2 although recent studies have presented evidence that it could also occur in PuO_2 (Haschke *et al.*, 2001).

Lindemer and Besmann (1985) presented a thermochemical model to represent the oxygen potential–temperature–composition data for $AnO_{2\pm x}$ assuming a solution of two fluorite structures with different O/An ratios. The reaction can be represented by

$$\left(\frac{2a}{b-2a}\right)\mathrm{AnO_2} + \mathrm{O_2} = \left(\frac{2}{b-2a}\right)\mathrm{An}_a\mathrm{O}_b \qquad (19.14a)$$

for the hyperstoichiometric range and

$$\left(\frac{2}{2a-b}\right)\mathrm{An}_a\mathrm{O}_b + \mathrm{O_2} = \left(\frac{2a}{2a-b}\right)\mathrm{AnO_2} \qquad (19.14b)$$

for the hypostoichiometric range. In these equations, An_aO_b is a hypothetical end-member of the fluorite solid solution $AnO_{2\pm x}$. The oxygen potential can then be represented by:

$$RT\ln(p\mathrm{O_2}) = \Delta_r H - T\Delta_r S + RTf(x) + Ef'(x) \qquad (19.15)$$

Table 19.8 *High-temperature heat capacity of the binary actinide oxides;* $C_p/(\mathrm{J\,K^{-1}\,mol^{-1}}) = a(\mathrm{T/K})^{-2} + b + c(\mathrm{T/K}) + d(T/K)^2 + e(\mathrm{T/K})^3 + f(\mathrm{T/K})^4$ (*estimated values are in italics*); *temperature T indicates the transition or melting temperatures except marked with m, when it indicates the maximum valid temperature of the polynomial equation.*

		a ($\times 10^{-6}$)	b	c ($\times 10^{3}$)	d ($\times 10^{6}$)	e ($\times 10^{9}$)	f ($\times 10^{12}$)	T (K)	$\Delta_{trs}H$ (kJ mol^{-1})	*References*
ThO_2	(cr)	–0.574031	55.9620	51.2579	–36.8022	9.2245		3651 ± 17	*82 ± 10*	a
	(liq)		61.76							a
UO_2	(cr)	–0.71391	52.1743	87.951	–84.2411	31.542	–2.6334	3110 ± 10	70 ± 4	b
	(l)	1328.8	0.25136							b
U_4O_9	(α)	–3.9602	319.163	49.691				348	2.594	c
	(β)	–3.9602	319.163	49.691				1400^m	11.9	c
U_3O_8	(cr)	–4.3116	279.267	27.480				2000^m		c
UO_3	(γ)	–1.00903	88.701	14.4896				1200^m		c
NpO_2	(cr)	–0.8969	73.662	8.8125				2820 ± 60	*63 ± 6*	d
PuO_2	(cr)	0.34759	36.2952	152.25	–127.255	36.289		2633 ± 40	*60 ± 10*	e
Pu_2O_3	(cr)	*–1.75053*	*130.6670*	*18.4357*				2358 ± 25	*113 ± 20*	e
AmO_2	(cr)	–1.9285	84.739	10.72	–0.8159			2000^m		c
Am_2O_3	(cr)	–1.071	113.93	59.37	–0.2301			1000^m		c
		–9.8742	153.13	3.573	2.372			2000^m		c
Cm_2O_3	(cr)	*–1.3489*	*123.532*	*14.550*				2543 ± 25		e
Bk_2O_3	(cr)							2196 ± 25		
Cf_2O_3	(cr)							*1875 ± 30*		

[a] Bakker *et al.* (1997).
[b] Fink (2000).
[c] NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[d] Fit of the estimated data by Serizawa *et al.* (2001).
[e] Konings (2004b).

where $f(x)$ and $f'(x)$ are functions of x that follow from the mass balance, and E is a temperature-dependent interaction energy term that was used in modeling the experimental data:

$$E = \Delta H_e - T\Delta S_e \tag{19.16}$$

Lindemer and Besmann (1985) analyzed the vast amount of experimental data and showed that hyperstoichiometric UO_{2+x} can be represented as a mixture of UO_2 and U_3O_7 for oxygen potentials above $RT\ln(p) = -266700 + 16.5(T/K)$, or $U_2O_{4.5}$ below this limit; hypostoichiometric UO_{2-x} as a mixture of UO_2 and the hypothetical end-member compound $U_{1/3}$. Besmann and Lindemer (1985, 1986) showed that PuO_{2-x} can be represented as a mixture of PuO_2 and $Pu_{4/3}O_2$.

Also for the Np–O, Am–O, Cm–O, Bk–O, and Cf–O systems, the $T-p(O_2)-x$ relations have been measured. The Np–O system was studied by Bartscher and Sari (1986) using the gas equilibrium technique, the other systems by Eyring and coworkers (Chikalla and Eyring, 1967; Turcotte *et al.*, 1971, 1973, 1980; Haire and Eyring, 1994) using oxygen decomposition measurements, and the Am–O system by Casalta (1996) using a galvanic cell. The data of most of these systems, however, do not allow a detailed description of the $T-p(O_2)-x$ relations due to insufficient knowledge of the composition of the solid phase. An exception is the Am–O system and Thiriet and Konings (2003) applied the Lindemer–Besmann approach to the results of Chikalla and Eyring (1967), showing that AmO_{2-x} can be represented as a mixture of $Am_{5/4}O_2$ and AmO_2.

19.5.3 Sesquioxides

(a) Enthalpy of formation

Unlike the 4f elements, for which sesquioxides are ubiquitous, only the sesquioxides of Ac and Pu through Es have been prepared (Haire and Eyring, 1994). Experimental data from solution calorimetry are available for Am_2O_3, Cm_2O_3, and Cf_2O_3 and the enthalpies of formation of these three compounds are well established (although by only one set of measurements). Their values, the former taken from the most recent assessments (Silva *et al.*, 1995; Konings, 2001b) and Cf_2O_3 from the original paper (Morss *et al.*, 1987), are given in Table 19.9.

As discussed for the dioxides, a systematic approach to the prediction of the enthalpies of formation of other sesquioxides can be made on the basis of the reaction enthalpy of the idealized dissolution reaction

$$An_2O_3(cr) + 6H^+(aq) \rightarrow 2An^{3+}(aq) + 3H_2O(l) \tag{19.17}$$

The enthalpy of this reaction can be used for establishing a relationship with molar volume, which was chosen as a parameter because there are three different sesquioxide structures with different coordination numbers and numbers of molecules per unit cell, as shown in Fig. 19.16. It is evident that, for all the three structure types, the enthalpies of solution of actinide sesquioxides are

Table 19.9 *Standard entropies and enthalpies of formation of the crystalline actinide and lanthanide sesquioxides; estimated values are in italics.*

An	$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*	*Ln*	$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*
Ac	*141.1 ± 5.0*	*–1756*	a	La	127.32	–1791.6 ± 2.0	c,f
Th				Ce	148.8	–1813.0 ± 2.0	c,f
Pa				Pr	*160.5*	–1809.9 ± 3.0	c,f
U	*176 ± 5.0*	*–1456*	a	Nd	158.45	–1806.9 ± 3.0	c,f
Np	*173 ± 5.0*	*–1522*	a	Pm	*158.0*	*–1811 ± 21*	c,f
Pu	163.02 ± 0.65	–1656 ± 10	b	Sm	150.62	–1823.0 ± 4.0	c,f
Am	*133.6 ± 5.0*	–1690.4 ± 8.0	b,c	Eu	*137.4*	–1650.4 ± 4.0	c,f
Cm	*167.0 ± 5.0*	–1684 ± 14	d	Gd	152.73	–1819.7 ± 3.6	c,f
Bk	*173.8 ± 5.0*	*–1694*	a	Tb	*159.2*	–1865.2 ± 6.0	c,f
Cf	*176.0 ± 5.0*	–1653 ± 10	a,e	Dy	149.78 ± 0.42	–1863.4 ± 5.0	c,f
Es	*180.0 ± 5.0*	*–1696*	a	Ho	158.16	–1883.3 ± 8.2	c,f
Fm		*–1694*	a	Er	153.13 ± 0.42	–1900.1 ± 6.5	c,f
Md		*–1535*	a	Tm	139.75	–1889.3 ± 5.7	c,f
No		*–1260*	a	Yb	133.05 ± 0.42	–1814.5 ± 6.0	c,f
Lr		*–1766*	a	Lu	109.96	–1877.0 ± 7.7	c,f

[a] Estimated in the present work.
[b] NEA-TDB (Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[c] Konings (2001b, 2002).
[d] Konings (2001a).
[e] Morss *et al.* (1987).
[f] Cordfunke and Konings (2001c).

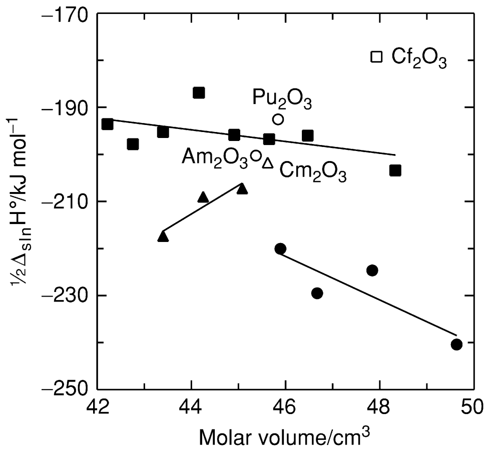

Fig. 19.16 *The enthalpy of solution* (*reaction* 19.17) *of the f-element sesquioxides; closed symbols, lanthanides; open symbols, actinides;* (•, ○), *hexagonal,* (▲, △), *monoclinic,* (■, □), *cubic.*

significantly less exothermic than for structurally similar lanthanide sesquioxides. With the exception of the enthalpy of formation of Pu_2O_3 (see below), the enthalpies of formation of the other sesquioxides were estimated from Fig. 19.16, taking in account their known or expected structural type.

Using the calculated enthalpies of formation of the sesquioxides of U and Np, it can be shown that these sesquioxides are thermodynamically unstable with respect to disproportionation to the metals and the much more stable dioxides, e.g. using enthalpies of formation and estimated entropies:

$$2Np_2O_3(c) = 3NpO_2(c) + Np(c), \quad \Delta G^\circ = -162 \text{ kJ mol}^{-1} \tag{19.18}$$

The corresponding U reaction has $\Delta G = -322$ kJ mol^{-1}. The case of Pu_2O_3 deserves special mention. Its enthalpy of formation has been estimated as $-(1710 \pm 13)$ kJ mol^{-1} (IAEA, 1967) from high-temperature EMF measurements, as $-(1685 \pm 21)$ kJ mol^{-1} (Chereau *et al.*, 1977) from high-temperature calorimetry, and as -1656 kJ mol^{-1} (Besmann and Lindemer, 1983) from earlier measurements and more recent heat capacity values. The last value is adopted in Lemire *et al.* (2001). Because there is an experimentally derived standard entropy of Pu_2O_3, we can calculate its Gibbs energy of reaction (19.17), -289 kJ mol^{-1}, for comparison with that of the structurally similar Nd_2O_3, -332 kJ mol^{-1}. Actinide sesquioxides appear to be more stable than structurally similar lanthanide sesquioxides in comparison with the corresponding aqueous solutions, so that nuclear waste oxide matrices that accept lanthanide ions should bind corresponding trivalent actinides (Pu^{3+}, Am^{3+}) even more strongly. The reason for this behavior is not clear; a rationalization is that the 5f covalence is stronger to oxygen in solid oxides than in hydrated ions.

Recommended values for the standard enthalpies of formation and entropies of the actinide and lanthanide sesquioxides are assembled in Table 19.9.

(b) Entropy

Low-temperature heat capacity measurements have been reported for Pu_2O_3 only (Flotow and Tetenbaum, 1981). This value was used to derive the entropies of Am_2O_3 and Cm_2O_3 (Konings, 2001a; Konings *et al.*, 2005) using equation (19.10), calculating the excess entropy from known crystal field energies. Because information on the lattice component in the actinide sesquioxide series is missing, and the lattice component was obtained by scaling the values derived from the isostructural lanthanide series (Fig. 19.17). In this series the lattice entropy can be described by a simple linear relation between La_2O_3 and Gd_2O_3, for which the lattice values are well known due to the f^0 and f^7 configurations.

(c) High-temperature properties

High-temperature properties of the actinide sesquioxides have hardly been studied. The phase transitions in the sesquioxides have been determined and it has been shown that the sesquioxides exhibit a polymorphism: bcc → monoclinic → hexagonal. The cubic to monoclinic transition is, however, irreversible, and the monoclinic form is thought to be the thermodynamically stable phase. The measured melting points of Pu_2O_3, Am_2O_3, Cm_2O_3, and Bk_2O_3 are plotted in Fig. 19.13 and show a maximum at Cm_2O_3.

The only measurements of high-temperature properties are for Pu_2O_3, Am_2O_3, Cm_2O_3, and Bk_2O_3. The most extensive are the studies made for $^{244}Cm_2O_3$,

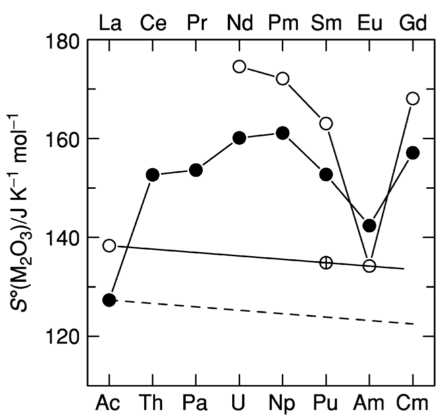

Fig. 19.17 *The entropy of the hexagonal/monoclinic lanthanide sesquioxides* (•), *showing the linear lattice component derived for the f^0 and f^7 configuration as a dotted line. The entropies of the actinide sesquioxides* (○) *are calculated for a parallel lattice component based on the Pu_2O_3 value* (⊕).

which was considered as an isotopic heat source in the 1970s. Vapor pressure studies (see Section 19.5.5) and thermal conductivity and thermal diffusivity measurements were reported. To convert the latter measurements to thermal conductivity, Gibby *et al.* (1970) estimated the heat capacity of Cm_2O_3. As discussed by Konings (2001a), these values are very high when compared to the lanthanide sesquioxide data. Since reliable high-temperature heat capacity data for the lanthanide sesquioxides are available, the functions of the actinide sesquioxides can be estimated from those by simple correlation (equation (19.13)).

19.5.4 Monoxides

Solid monoxides of Th and of U through Am have been reported as surface layers on the metals, as the reduction product of PuO_2 with Pu or C, or as the product of reaction of Am with HgO. However, these solid 'monoxides' may be oxycarbides (Larson and Haschke, 1981). Usami *et al.* (2002) claim the formation of AmO by lithium reduction of AmO_2. The product was, however, not characterized but its formation was deduced from a mass balance. The authors estimated its Gibbs energy of formation as -481.1 kJ mol^{-1} at 923 K.

Among the reported lanthanide monoxides, only EuO is well characterized, impure YbO can be prepared with difficulty, and 'metallic' (trivalent) monoxides of La, Ce, Pr, Nd, and Sm can be synthesized at high temperature and pressure. Earlier reports of lanthanide monoxides as surface phases are believed to be oxynitrides, oxycarbides, or hydrides (Morss, 1983). Thermodynamic calculations have shown how marginally stable the few lanthanide monoxides are, even under the exotic conditions of their preparation, and that classical (divalent) CfO should be unstable with respect to disproportionation (Morss, 1983). Thus the only hope of synthesis of actinide monoxides would appear to be the high-pressure route for AmO and CfO, an extremely demanding synthetic procedure.

19.5.5 Oxides in the gas phase

Gaseous actinide oxide molecules of the types AnO, AnO_2, and AnO_3 have all been identified in Knudsen cell effusion or matrix isolation experiments of vapors above the solid oxides. The experimental work is restricted to the oxides of Th to Cm.

Thorium dioxide principally vaporizes to give ThO_2 molecules. Numerous vapor pressure studies have been performed for the solid–gas equilibrium, none of them, however, with techniques to confirm the vapor composition. Ackermann and Rauh (1973a) as well as Belov and Semenov (1980) reported the existence of the monoxide ThO in the vapor phase using mass spectrometry. Ackermann and Rauh (1973b) derived enthalpies of formation of the two molecules from the existing studies by correcting the vapor pressure studies for the ThO contribution. The thermal functions of the gaseous molecules have been calculated from molecular parameters (Rand, 1975). The properties of the ThO molecule are based on experimental results as summarized by Rand (1975) and have been confirmed by quantum chemical calculations (Küchle *et al.*, 1994). ThO_2 is a bent molecule, as was derived from matrix-isolation and molecular beam deflection studies (Linevsky, 1963; Kaufman *et al.*, 1967; Gabelnick *et al.*, 1974).

In the Pa–O system the monoxide and dioxide species have been identified in the vapor above PaO_{2-x} (Kleinschmidt and Ward, 1986) and above Pa metal in the presence of small amounts of oxygen (Bradbury, 1981).

The situation for uranium is more complex. The binary molecules UO, UO_2, and UO_3 coexist above solid and liquid UO_2, and at very high temperatures even dimeric molecules of these species and ionic species contribute to the vapor pressure. The UO_2 molecule does not have a bent structure, like ThO_2, but is linear; UO_3 is planar with a T-shaped geometry (Green, 1980). The relative fractions of these species are highly dependent on the temperature and O/U ratio of the condensed phase. Ronchi *et al.* (2002) have presented a detailed analysis of these complex equilibria, for which a large number of studies has been made up to very high temperatures, and their recommended values for the enthalpies of formation and entropies are listed in Table 19.10.

Ackermann *et al.* (1966a) measured the vapor pressure of NpO_2 by the Knudsen effusion technique. Mass spectrometric measurements confirmed that NpO_2 is the dominant vapor species but that NpO(g) also has a significant contribution to the vapor. Ackermann and Rauh (1975) studied the isomolecular

Table 19.10 *Thermodynamic properties of the gaseous polyatomic actinide oxides; estimated values are in italics.*

	$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*
UO_3	309.5 ± 2.0	–795.0 ± 10.0	a
ThO_2	281.7 ± 4.0	–455.2 ± 10.0	b
UO_2	266.4 ± 4.0	–476.2 ± 10.0	a
NpO_2	276.5 ± 5.0	–444 ± 20	e
PuO_2	278.0 ± 5.0	–410 ± 20	c
ThO	240.1 ± 2.0	–20.9 ± 10.0	b
UO	248.8 ± 2.0	24.7 ± 10.0	a
NpO	257.9 ± 5.0	−9 ± 5	e
PuO	248.1 ± 3.0	–60.0 ± 10.0	c
CmO	261.9 ± 10.0	–175 ± 15	d

[a] Ronchi *et al.* (2002).
[b] IVTAN-THERMO Database of the Institute for High Temperatures of the Russian Academy of Sciences.
[c] Glushko *et al.* (1978).
[d] Konings (2002).
[e] Ackermann *et al.* (1966a).

exchange reactions with La and Y by mass spectrometry. In addition, Ackermann and Rauh (1975) studied the NpO vapor pressure over the univariant system (NpO_2(cr)+Np(l)+vapor) by Knudsen effusion technique. This approach yields results that are within the limits of uncertainty of the analysis of the isomolecular exchange reactions. The selected enthalpies of formation are derived from these studies.

In the Pu–O system, it has been thought for a long time that only PuO_2 and PuO exist as binary molecular species, but recently the existence of the PuO_3 molecule has been reported (Ronchi *et al.*, 2000). Matrix-isolation spectroscopy (Green and Reedy, 1978a,b) has established the linear molecular structure of PuO_2 and yielded values for the vibrational stretching frequencies. Archibong and Ray (2000) calculated the molecular properties of PuO_2 using quantum chemical techniques. They found that the $^5\Sigma_g^+$ and the $^5\Phi_u$ states are both candidates for the ground state, being almost equal in energy, the former preferred because of somewhat better agreement with the experiments for the two stretching frequencies. However, the data for the internuclear distance and the bending frequency for the $^5\Sigma_g^+$ state differ considerably from the estimates by Green (1980) on basis of the UO_2 data, whereas the data for the $^5\Phi_u$ state agree reasonably. The enthalpies of formation of PuO and PuO_2 are taken from Glushko *et al.* (1978).

The vapor pressure of americium oxides has been deduced from measurements of plutonium oxides containing small amounts of ^{241}Am as decay product using Raoult's law (Ackermann *et al.* 1966b; Ohse, 1968). Although no direct measurement of the vapor species was made in either study, it was assumed that the AmO and AmO_2 molecules are present. These data do not, however, allow the derivation of formation properties.

For the Cm–O system, Knudsen cell effusion measurements have been performed (Smith and Peterson, 1970) from which it was concluded that Cm_2O_3 vaporizes according to the reaction:

$$Cm_2O_3(cr,l) = 2\,CmO(g) + O(g) \tag{19.19}$$

which is analogous to the lanthanide sesquioxides. Hiernaut and Ronchi (2004) recently measured the vapor pressure of $(Cm,Pu)_2O_3$ by Knudsen effusion mass spectrometry, confirming the results and conclusions of Smith and Peterson (1970).

The dissociation energy of the actinide monoxides are plotted in Fig. 19.18 together with those of the lanthanide monoxides (Pedley and Marshall, 1983). The pattern that emerges for the actinide monoxides is parallel to that of the lanthanide monoxides and the dissociation energies of AmO can be estimated. Haire (1994) discussed this pattern in more detail, and extended the estimates to the heaviest actinides. He described the dissociation energy by a base energy $D_{0,\mathrm{base}}$ and a ΔE value (as proposed by Murad and Hildenbrand (1980)):

$$D_0 = D_{0,\mathrm{base}} + \Delta E \tag{19.20}$$

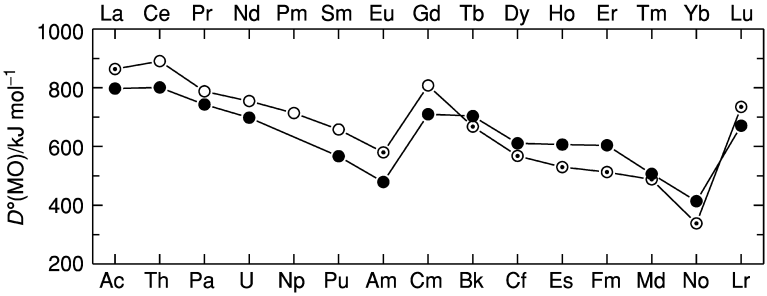

Fig. 19.18 *Dissociation energy of lanthanide* (•) *and actinide* (○) *monoxides; estimated values* (*see text*) *are indicated by* (⊙).

A ds-state was assumed for these molecules, which means that a promotion energy of a f-electron to a d-state is required. This is the origin of the ΔE value, which can be derived from theoretical calculation (Brooks *et al.*, 1984). The $D_{0\ \mathrm{base}}$ value was represented by interpolation of the LaO–GdO–LuO line, i.e. those lanthanides that already have one d-electron. In transposing this relationship to the actinides, Haire assumed that the base relation is the same in the 4f and 5f series but the value for CmO adopted here (the actinide analog of GdO) suggests that there is a systematic difference of about 70 kJ mol^{-1} (Fig. 19.18). We have corrected Haire's values for this difference and the data for the monoxides beyond CmO thus obtained are shown in Fig. 19.18.

Recently Santos *et al.* (2002a,b) suggested that the excited 'bonding' state is obtained by promotion of an s-electron to a d-level to create the double bond. The lowest-lying excited states to be considered are $4f^{n-3}5d^26s$ and $4f^{n-2}5d6s$. Gibson (2003) showed how the energy required to promote gaseous lanthanide atoms to the excited 'bonding' state is responsible for the trends in the LnO dissociation energies. He defined the intrinsic Ln=O bond energy as "the bonding interaction between an oxygen atom and a lanthanide atom, Ln*, that has an electron configuration suitable for formation of the covalent formally double bond in the Ln=O molecule." He identified the $4f^{n-3}5d^26s$ configuration as the appropriate one for bonding and the two 5d electrons as the electrons that provide bonding with the oxygen. Thus the trend was explained as:

$$D^0(\mathrm{LnO}) = D^{0*}(\mathrm{LnO}) = \Delta E\ [\text{ground} \rightarrow \text{bonding configuration}] \qquad (19.21)$$

19.5.6 Complex oxides

(a) Ternary and quaternary oxides with alkali metal ions

An extensive number of thermodynamic studies of the alkali uranates have been reported and the existing thermochemical data have been assessed by Cordfunke and O'Hare (1978) and Grenthe *et al.* (1992), the latter study updated by Guillaumont *et al.* (2003). These thermochemical data are, however, much fewer than the large number of phases existing in the A_2O–UO_3–UO_2 phase diagrams (Lindemer *et al.*, 1981). And no thermodynamic studies exist for ternary compounds with the alkali ions containing tetravalent actinide ions. Thermochemical measurements have also been reported for a few ternary oxides of alkali metals and Np(VI). No thermochemical measurements have been reported for compounds of the alkali metal with other actinide oxides, surprisingly not even for the sodium plutonates.

(*i*) *Enthalpy of formation*

The enthalpies of formation of the alkali uranates are generally derived from enthalpy of solution measurements in hydrochloric or nitric acid, often involving very complex reaction cycles to compensate the oxidation of uranium. The measurements have been made for mixed compounds of the general formulas $nA_2O \cdot mUO_3$ (hexavalent U) and $nA_2O \cdot mUO_{2.5}$ (pentavalent U). All existing literature have been reviewed by Grenthe *et al.* (1992) and Guillaumont *et al.* (2003) using currently accepted auxiliary data. Johnson (1975) as well as Lindemer *et al.* (1981) discussed correlations and methods to estimate unknown enthalpies of formation for the complex alkali uranates up to high n/m ratios (e.g. $Cs_2O \cdot 15UO_3$), but their procedures are quite arbitrary.

For the alkali metal neptunates(VI) with the general formulas A_2NpO_4, $A_2Np_2O_7$, and A_4NpO_5, the enthalpies of formation were derived from the enthalpies of solution of the compounds in hydrochloric acid. These results were recently assessed by Lemire *et al.* (2001). The values of the enthalpies of formation of all these compounds are given in Table 19.11.

(*ii*) *Entropy*

Only a few low-temperature heat capacity measurements have been made for the alkali uranates, and they are restricted to sodium and cesium compounds (see Table 19.11). Lindemer *et al.* (1981) estimated the entropy values for the other alkali uranates assuming that $\Delta_r S$ for the formation reaction from the oxides is zero. The experimental results show that this is not the case and that the values for $\Delta_r S$ strongly depend on the crystallographic modification and tend to be slightly positive. For these reasons, the values by Lindemer *et al.* (1981) have not been included in the present tabulations.

(*iii*) *High-temperature properties*

High-temperature enthalpy increment measurements have been made for a few alkali uranates. These are essentially the same compounds for which low-temperature measurements have been performed. Most of the early data have been reviewed by Cordfunke and O'Hare (1978) and Cordfunke and Konings (1990) and they are summarized in Table 19.13. In the 1990s, the

Table 19.11 *Entropies and enthalpies of formation of crystalline complex alkali actinide oxides, from NEA-TDB* (*Grenthe* et al., 1992; *Lemire* et al., 2001; *Guillaumont* et al., 2003); *see text for explanation.*

	Li		*Na*		*K*		*Rb*		*Cs*	
	S° (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$ (298.15 K) (kJ mol^{-1})	S° (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$ (298.15 K) (kJ mol^{-1})	S° (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$ (298.15 K) (kJ mol^{-1})	S° (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$ (298.15 K) (kJ mol^{-1})	S° (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H^\circ$ (298.15 K) (kJ mol^{-1})
M_4UO_5	133.0 ± 6.0	–2639.4 ± 1.7		–2457.0 ± 2.2[a]						
M_2UO_4		–1968.2 ± 1.3	166.0 ± 0.5[b]	–1897.7 ± 3.5[b] –1884.6 ± 3.6[a]	*180 ± 8*	–1920.7 ± 2.2	*203 ± 8*	–1922.7 ± 2.2	219.66 ± 0.44	–1928.0 ± 1.2
MUO_3		–1522.3 ± 1.8	132.84 ± 0.40	–1494.9 ± 10.0		–1522.9 ± 1.7		–1520.9 ± 1.8		
$M_2U_2O_7$		–3213.6 ± 5.3	275.9 ± 1.0	–3203.8 ± 4.0		–3250.5 ± 4.5		–3232.0 ± 4.3	327.75 ± 0.66	–3220 ± 10
$M_2U_3O_{10}$		–4437.4 ± 4.1								
$M_2U_4O_{12}$									526.4 ± 3.5	–5571.8 ± 3.6
M_3UO_4			198.2 ± 0.4	–2024 ± 8						
$M_6U_7O_{24}$				–10841.7 ± 10.0						
M_2NpO_4		–1828.2 ± 5.8		–1763.8 ± 5.7[b] –1748.5 ± 6.1[a]		–1784.3 ± 6.4				–1788.1 ± 5.7
$M_2Np_2O_7$				–2894 ± 11		–2932 ± 11		–2914 ± 12		
M_4NpO_5				–2315.4 ± 5.7[a]						

[a] Beta form.
[b] Alpha form.

Indian group led by Venugopal and coworkers measured the enthalpy increments of a number uranates of potassium, rubidium, and cesium. They were reviewed by Guillaumont *et al.* (2003), and some of their recommendations have been included in Table 19.13.

(b) Ternary and quaternary oxides with alkaline-earth ions

(*i*) *Enthalpy of formation*

The following perovskites with alkaline-earth ions containing tetravalent actinide ions have been studied thermodynamically: $BaUO_3$ (Williams *et al.*, 1984; Cordfunke *et al.*, 1997), $BaPuO_3$ (Morss and Eller, 1989), $BaAmO_3$ and $SrAmO_3$ (Goudiakas *et al.*, 1990), $BaCmO_3$, and $BaCfO_3$ (Fuger *et al.*, 1993). Efforts to obtain the strontium analog of $BaUO_3$, $SrUO_3$, resulted in a perovskite phase with the empirical formula $Sr_2UO_{4.5}$ (crystallographic formula $Sr_2(Sr_{2/3}U_{1/3})UO_6$) (Cordfunke and IJdo, 1994). Also $BaUO_3$ cannot be prepared with a Ba/U ratio of exactly 1, as was found independently by Barrett *et al.* (1982), Williams *et al.* (1984), and Cordfunke *et al.* (1997). The latter two groups determined the enthalpy of the ideal composition by extrapolating the data for different Ba/U ratios and found excellent agreement [$-(1690 \pm 10)$ kJ mol^{-1} and $-(1680 \pm 10)$ kJ mol^{-1}]. However, there are several reports of studies on materials claimed to be $SrUO_3$ and $BaUO_3$. Huang *et al.* (1997a) derived the enthalpy of formation of $SrUO_{3.1}$ from Knudsen effusion mass spectrometric measurements. Ali *et al.* (2001) used a comparable method (but a complex reaction) for $SrThO_3$.

Using the Goldschmidt tolerance factor t, expressed as $t = (R_{Ba} + R_O)/(2^{1/2})(R_{An} + R_O)$, where R_{Ba}, R_O, and R_{An} represent the ionic radii of Ba^{2+}, O^{2-}, and the actinide 4+ ion, respectively, Morss and Eller (1989) showed that the enthalpy of formation of the complex oxides from BaO and AnO_2 becomes less favorable as t decreases. This correlation was extended by Fuger *et al.* (1993) to a large number of complex oxides of the general formula $MM'O_3$ ($M = Ba$, and $M' = Ti$, Hf, Zr, Ce, Tb, U, Pu, Am, Cm, and $M = Sr$, and $M' =$ Ti, Mo, Zr, Ce, Tb, Am) and allowed the prediction of the enthalpy of formation of yet unprepared actinide(IV) complex oxides with BaO and SrO. This correlation was in accordance with the inability to obtain stoichiometric $BaUO_3$.

Cordfunke *et al.* (1997) suggested that a continuous series exists between $BaUO_3$–$Ba_{1+y}UO_{3+x}$–Ba_3UO_6. The oxidation of U^{4+} ions is accompanied by the formation of metal vacancies on the Ba and U sites, and Ba substitution on the U-vacancies, finally resulting in $Ba_2(Ba,U)O_6$. $Ba_2U_2O_7$ does not belong to this series, which is explained by the fact that $Ba_2U_2O_7$ is a complex oxide containing pentavalent uranium. For the system Sr–U–O it was shown by Cordfunke *et al.* (1999) that the enthalpies of formation of the U(VI) compounds linearly depend on the Sr/U ratio (Fig. 19.19). The data fall into two groups, the pseudo-hexagonal types ($Sr_3U_{11}O_{36}$, $Sr_2U_3O_{11}$, $SrUO_4$, and UO_3) and the perovskite types ($Sr_5U_3O_{14}$, Sr_2UO_5, Sr_3UO_6). Takahashi *et al.* (1993) studied the enthalpies of formation of $SrUO_{4-y}$ ($0 \leq y \leq 0.5$) also finding an almost linear relationship.

Complex oxides of the formula $n\mathrm{AO} \cdot m\mathrm{AnO}_3$ with alkaline-earth ions containing hexavalent actinides are well known. AUO_4 compounds have been identified and thermochemically characterized for magnesium, calcium, strontium, and barium. Also the enthalpies of formation of many A_3AnO_6 (An = U, Np, Pu) and quaternary $Ba_2A'AnO_6$ (A′ = Mg, Ca, Sr and An = U, Np, Pu) compounds have been determined (see Table 19.12). All the values listed have been taken from the NEA assessments (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003) except for those on curium and californium compounds (Fuger *et al.*, 1993).

The enthalpy of formation from the binary oxides, here called the enthalpy of complexation $\Delta_{\mathrm{cplx}}H$, is an excellent measure for the stability of these compounds. It can be calculated easily for the uranates, but not for complex Np(VI) oxides or for complex Pu(VI) oxides, because NpO_3(c) and PuO_3(c) are unknown. For the construction of Fig. 19.20, we have therefore utilized the value estimated in Section 19.5.1. The exothermic enthalpy effect of the reactions indicated in Fig. 19.20 implies that the compounds are thermodynamically stable at room temperature, assuming a negligible entropy change upon the formation of the complex oxides from the binary oxides. Extrapolation of the trends indicated that the beryllium compounds are not stable under these conditions.

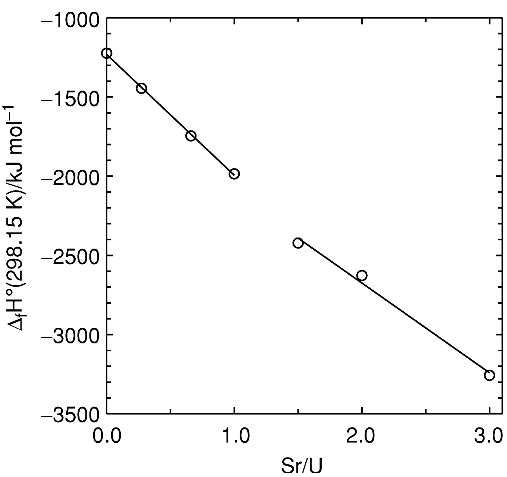

Fig. 19.19 *The enthalpy of formation in the strontium uranates in the Sr–U*$^{\mathrm{VI}}$*–O system* (*after Cordfunke* et al., 1999).

Table 19.12 *Entropies and enthalpies of formation of crystalline complex alkaline-earth actinide oxides, from NEA-TDB* (*Grenthe* et al., 1992; *Silva* et al., 1995; *Lemire* et al., 2001; *Guillaumont* et al., 2003) *except for those on curium and californium compounds* (*Fuger* et al., 1993).

	Mg		*Ca*		*Sr*		*Ba*	
	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})
MUO_3						–1672.6 ± 8.6		–1690 ± 10
MUO_4	131.95 ± 0.17	–1857.3 ± 1.5	121.1 ± 0.17	–2002.3 ± 2.3	153.15 ± 0.17[a]	–1989.6 ± 2.8[a] –1988.4 ± 5.4[b]	153.97 ± 0.31	–1993.8 ± 3.3
MU_2O_7							*260 ± 15*	–3237.2 ± 5.0
MU_3O_{10}	338.6 ± 1.0							
$M_2UO_{4.5}$						–2494.0 ± 2.3		
MU_4O_{13}						–5920 ± 20		
M_2UO_5						–2632.9 ± 1.9		
$M_2U_2O_7$							*296 ± 15*	–3740.0 ± 6.3
$M_2U_3O_{11}$						–5243.7 ± 5.0		
M_3UO_6				–3305.4 ± 4.1		–3263.4 ± 3.0	*298 ± 15*	–3210.4 ± 8.0
Ba_2MUO_6		–3245.9 ± 6.5		–3295.8 ± 5.9		–3257.3 ± 5.7		
$M_3U_2O_9$						–4620.0 ± 8.0		
$M_3U_{11}O_{36}$						–15903.8 ± 16.5		
$M_5U_3O_{14}$						–7248.6 ± 7.5		
M_3NpO_6						–3125.8 ± 5.9		–3085.6 ± 9.6
Ba_2MNpO_6		–3096.9 ± 8.2		–3159.3 ± 7.9		–3122.5 ± 7.8		
$MPuO_3$								–1654.2 ± 8.3
M_3PuO_6						–3042.1 ± 7.9		–2997 ± 10
Ba_2MPuO_6		–2995.8 ± 8.8		–3067.5 ± 8.9		–3023.3 ± 9.0		
$MAmO_3$						–1539.0 ± 7.9		–1544.6 ± 3.4
$MCmO_3$								–1517.8 ± 7.1
$MCfO_3$								–1477.9 ± 5.6

[a] Alpha form (rhombohedral).
[b] Beta form (orthorhombic).

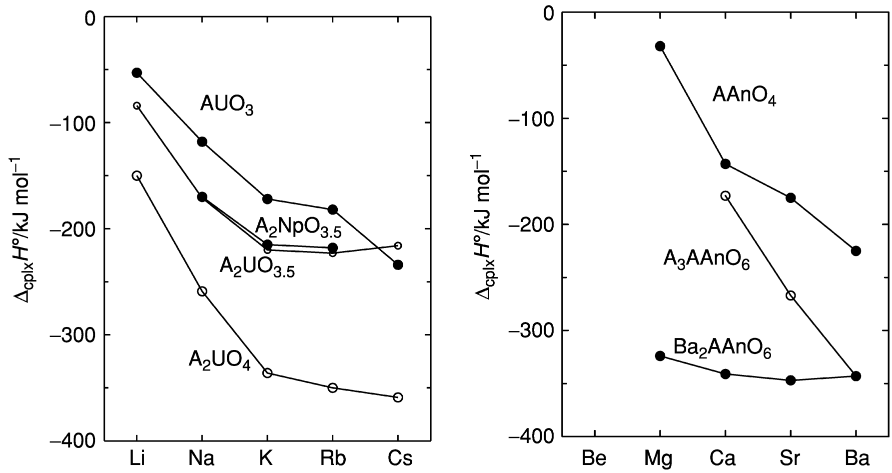

Fig. 19.20 *Enthalpies of complexation of complex actinide*(VI) *oxides where A represents a alkali or alkaline earth and An an actinide ion.*

There are, as of the time of writing, no thermochemical data on complex oxides containing trivalent actinides (e.g. $AmAlO_3$ or $SrAm_2O_4$). Indeed, such measurements are still lacking for the lanthanides.

(*ii*) *Entropy*

Low-temperature heat capacity measurements have been reported for a few alkaline-earth uranates. The data for the AUO_4 monouranates of the series A = Mg to Ba (Table 19.12) need some further discussion. The two measurements for $BaUO_4$ are discordant, though made by well-known research groups. The results of Westrum *et al.* (1980) give $S°(298.15\ K) = 177.84\ J\ K^{-1}\ mol^{-1}$ whereas the results of O'Hare *et al.* (1980) gave 153.97 J K^{-1} mol^{-1}. In most assessments the latter value is selected because the sample was better characterized. However, the values for the other alkaline-earth monouranates are from the same set of measurements by Westrum *et al.* (1980) and the reported data indicate a regular trend with molar volume for the orthorhombic compounds (A = Mg, Sr, Ba). The value of O'Hare *et al.* (1980) does not fit in the series, which would imply that the values for the other compounds measured by Westrum *et al.* (1980) are in error, which is not considered in the NEA-TDB selections (Grenthe *et al.*, 1992). Another way of looking at this problem is to consider the entropy of complexation from the oxides. The values for the orthorhombic monouranates derived from the measurements of Westrum *et al.* (1980) all suggest that the quantity $\Delta_{cplx}S°(298.15\ K)$ is positive which is the case for most orthorhombic complex oxides. The result for $BaUO_4$ from O'Hare *et al.* (1980) in contrast, suggests a negative value. Clearly further measurements are required to solve this problem.

(*iii*) *High-temperature properties*

High-temperature heat capacity data have been measured for the AUO_4 compounds of the series A = Mg to Ba and have been evaluated by Cordfunke and O'Hare (1978); the resulting recommended equations are summarized in Table 19.13. They agree with the less exhaustive selections of the NEA assessment (Grenthe *et al.*, 1992). Melting points of these compounds are not known. The high-temperature properties of the other alkaline-earth compounds are poorly known. Recently, Japanese researchers have extensively studied materials claimed to be stoichiometric $BaUO_3$ and $SrUO_3$. The heat capacity (Matsuda *et al.*, 2001), thermal expansion, thermal conductivity and melting point (Yamanaka *et al.*, 2001), and the vaporization behavior (Huang *et al.*, 1997a) were measured. Vaporization measurements have also been made for $SrUO_3$ (Huang *et al.*, 1997b) and $BaPuO_3$ (Nakajima *et al.*, 1999b). Dash *et al.* (2000) reported enthalpy increments of $Sr_3U_{11}O_{36}$ and $Sr_3U_2O_9$. The relevant thermodynamic data extracted from these studies are listed in Table 19.12.

(c) Other ternary and quaternary oxides/oxysalts

Enthalpies of formation data for uranium carbonates, nitrates, phosphates, arsenates, and silicates have been measured and the available data were reviewed and summarized in the NEA-TDB assessments (Grenthe *et al.*, 1992; Guillaumont *et al.*, 2003). Heat capacity and entropy data have hardly been measured for these compounds and only estimates are available. The data are summarized in Table 19.14. Also included are the enthalpies of formation of several actinide (Th,U) bearing mineral phases reported by Helean *et al.* (2002, 2003) and by Mazeina *et al.* (2005) using high temperature solution calorimetry. Data for complex oxides or oxyacids of other actinides are not known with sufficient accuracy for inclusion in this chapter.

19.6 HALIDES

Because of the fundamental and applied interest in the many actinide halides, their thermodynamic properties have received much attention. The authoritative assessment by Fuger *et al.* (1983), which formed the basis for the data in the second edition of this work, is still the major source of information though parts of it have been updated in the NEA-TDB series on *Chemical Thermodynamics* (U through Am).

Table 19.13 *High-temperature heat capacity of selected crystalline complex actinide oxides;* $C_p/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a(\mathrm{T/K})^{-2} + b + c(\mathrm{T/K}) + d(\mathrm{T/K})^2$ (*estimated values are in italics, maximum temperatures in brackets*).

		a ($\times10^{-6}$)	b	c ($\times10^{3}$)	d ($\times10^{6}$)	T (K)	ΔH (kJ mol^{-1})	*References*
$NaUO_3$		–1.0966	115.491	19.1672		[1000]		a
Na_2UO_4	(α)	–2.09664	162.5384	25.8857		1193	20.92	b
	(β)		224.6743					b
Na_3UO_4		–2.08007	188.901	25.1788				c
$Na_2U_2O_7$	(α)	–3.54904	262.831	14.6532				a
	(β)		280.571					a
KUO_3			133.258	12.558		[800]		d
$K_2U_2O_7$			149.084	269.5		[800]		d
Cs_2UO_4		–1.52851	164.8814	17.0232				c
$Cs_2U_2O_7$		–1.13403	221.532	75.3158				c
$Cs_2U_4O_{12}$		–5.4375	423.7262	71.9406				c
$MgUO_4$			110.2681	66.7959	23.4381			b
$CaUO_4$	(α)		115.6039	46.819		1025	0.920	b
	(β)		113.0100	52.6347				b
$SrUO_4$	(α)	0.64475	102.7703	69.0394				c
$Sr_3U_2O_9$		–4.6201	319.18	116.02				e
$Sr_3U_{11}O_{36}$		–0.3954	962.72	355.26		[1000]		e
$BaUO_4$		–2.7776	153.7812	9.1788				c
$BaUO_3$		–0.142	126.6	16.1		2450		f

[a] Cordfunke *et al*. (1982).
[b] Cordfunke and O'Hare (1978).
[c] Cordfunke and Konings (1990).
[d] Guillaumont *et al*. (2004).
[e] Dash *et al*. (2000).
[f] Matsuda *et al*. (2001); Yamanaka *et al*. (2001).

Table 19.14 *Thermodynamic properties of selected crystalline miscellaneous actinide oxyacids and oxysalts.*

	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
$Th(NO_3)_4$		–1445.6 ± 12.6	a
$Th(NO_3)_4 \cdot 4H_2O$		–2707.0 ± 12.6	a
$Th(NO_3)_4 \cdot 5H_2O$	543.1 ± 0.4	–3007.9 ± 4.2	a
$ThTi_2O_6$		–3096.5 ± 4.3	b
$ThSiO_4$ (thorite)		–2117.6 ± 4.2	b
$ThSiO_4$ (huttonite)		–2110.9 ± 4.7	b
UO_2CO_3	144.2 ± 0.3	–1691.3 ± 1.8	c
$UO_2(NO_3)_2$	*241 ± 9*	–1351.0 ± 5.0	c
$UO_2(NO_3)_2 \cdot 2H_2O$	*327.5 ± 8.8*	–1978.7 ± 1.7	c
$UO_2(NO_3)_2 \cdot 3H_2O$	*367.9 ± 3.3*	–2280.4 ± 1.7	c
$UO_2(NO_3)_2 \cdot 6H_2O$	505.6 ± 2.0	–3167.5 ± 1.5	c
$UO_3 \cdot 1/2NH_3 \cdot 1\frac{2}{3}H_2O$		–1770.3 ± 0.8	a
$UO_3 \cdot \frac{1}{2}NH_3 \cdot 1\frac{1}{2}H_2O$		–1741.3 ± 0.8	a
$UO_3 \cdot \frac{2}{3}NH_3 \cdot 1\frac{1}{3}H_2O$		–1705.8 ± 0.8	a
$USiO_4$	*118 ± 12*	–1991.3 ± 5.4	c
$U_{0.97}Ti_{2.03}O_6$		–2977.9 ± 3.5	b
$Ca_{1.46}U_{0.69}Ti_{1.85}O_7$		–3610.6 ± 4.1	b
$(UO_2)_3(PO_4)_2$	*410 ± 14*	–5491.3 ± 3.5	c
$(UO_2)_2P_2O_7$	*296 ± 21*	–4232.6 ± 2.8	c
UPO_5	*137 ± 10*	–2064 ± 4	c
UP_2O_7	*204 ± 12*	–2852 ± 4	c
UO_2SO_4	*163.2 ± 8.4*	–1845.1 ± 0.84	c
$UO_2SO_4 \cdot 2.5H_2O$	*246.1 ± 6.8*	–2607.0 ± 0.9	c
$UO_2SO_4 \cdot 3H_2O$	*274.1 ± 16.6*	–2751.5 ± 4.6	c
$UO_2SO_4 \cdot 3.5H_2O$	*286.5 ± 6.6*	–2901.6 ± 0.8	c
$U(SO_4)_2$	*180 ± 21*	–2309.6 ± 12.6	c
$U(SO_4)_2 \cdot 4H_2O$	*359 ± 32*	–3483.2 ± 6.3	c
$U(SO_4)_2 \cdot 8H_2O$	*538 ± 52*	–4662.6 ± 6.3	c
$(UO_2)_3(AsO_4)_2$	*387 ± 30*	–4689.4 ± 8.0	c
$(UO_2)_2As_2O_7$	*307 ± 30*	–3426.0 ± 8.0	c
$UO_2(AsO_3)_2$	*231 ± 30*	–2156.6 ± 8.0	c
$NpO_2(NO_3)_2 \cdot 6H_2O$	*516.3 ± 8.0*	–3008.2 ± 5.0	c
$PuTi_2O_6$		*–2909 ± 8*	b

[a] Cordfunke and O'Hare (1978).
[b] Helean *et al.* (2002, 2003); Mazeina *et al.* (2005).
[c] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

19.6.1 Hexahalides

(a) Solid hexahalides

The enthalpy of formation of UF_6 is a key value for the U–F thermochemistry. This value is well established by fluorine combustion calorimetry (Johnson, 1979). The heat capacity of UF_6 has been measured accurately up to the melting point and beyond (Brickwedde *et al.*, 1948), from which the entropy can be

Table 19.15 *Thermodynamic properties of the crystalline hexa- and pentahalides at 298.15 K; estimated vales are given in italics.*

	C_p(298.15 K) (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
UF_6	166.8 ± 0.2	227.6 ± 1.3	–2197.7 ± 1.8	a
UCl_6	175.7 ± 4.2	285.5 ± 1.7	–1066.5 ± 3.0	a
NpF_6	167.44 ± 0.40	229.09 ± 0.50	*–1970 ± 20*	a
PuF_6	*168.1 ± 2.0*	221.8 ± 1.1	*–1861 ± 20*	a
$PaCl_5$	–	*238 ± 8*	–1147.8 ± 14.4	b
$PaBr_5$	–	*289 ± 17*	–866.8 ± 14.9	b
$UF_5(\alpha)$	132.2 ± 4.2	199.6 ± 3.0	–2075.3 ± 5.9	a
$UF_5(\beta)$	*132.2 ± 12.0*	*179.5 ± 12.6*	–2083.2 ± 4.2	a
UCl_5	*150.6 ± 8.4*	*242.7 ± 8.4*	–1039.0 ± 3.0	a
UBr_5	*160.7 ± 8.0*	*292.9 ± 12.6*	–810.4 ± 8.4	a
NpF_5	*132.8 ± 8.0*	*200 ± 3*	*–1941 ± 25*	a

[a] NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[b] Fuger *et al.* (1983) taking in account the enthalpy of dissolution of the standard state of the metal (Fuger *et al.*, 1978) and more recent auxiliary values.

derived. The resulting values are summarized in Table 19.15. Unfortunately the situation is different for NpF_6 and PuF_6. Low-temperature heat capacity measurements have been made for NpF_6, also into the liquid range, but a determination of its enthalpy of formation is lacking. Lemire *et al.* (2001) derived this quantity from the estimated difference $\{\Delta_f H°(MF_6, cr) - \Delta_f H°(MO_2^{2+}, aq)\}$ obtained by interpolation in the AnF_6 series. For PuF_6, no thermodynamic measurements of the solid phase have been made except for the vapor pressure. But since the properties of the gas phase are well established (see below), the enthalpy of formation and the standard entropy can be derived with reasonable accuracy.

UCl_6 is the only known solid actinide hexachloride. Its thermochemical properties were intensely studied in the World War II period. Thereafter Gross *et al.* (1971) and Cordfunke *et al.* (1982) performed enthalpy-of-solution studies on this compound and derived the enthalpy of formation. As discussed by Grenthe *et al.* (1992) the values for UCl_6 from these two studies disagree (unlike similar work for UCl_5) and the results of Cordfunke *et al.* (1982) were selected. The heat capacity and entropy for UCl_6 at low temperature were measured by Ferguson and Rand in the early 1940s, as reported in Katz and Rabinowitch (1951); the high-temperature heat capacity of UCl_6 is an estimate by Barin and Knacke (1973).

The high-temperature heat capacity equations plus the melting data of the hexahalides are summarized in Table 19.16.

(b) Gaseous hexahalides

The gaseous hexafluorides of U, Np, and Pu were studied extensively in the 1950s and 1960s. Gas-phase electron diffraction, Raman, and infrared studies have established the octahedral structure (O_h symmetry) and the molecular and vibrational parameters. From these data the entropies can be calculated accurately; the major uncertainty coming from neglect of excited electronic states for incompletely filled f-shells. The enthalpies of formation of these species can then be obtained from analyses of the vapor pressure measurements that have been performed and such data have been derived in the NEA-TDB series (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003). The molecular properties of AmF_6, and thus the entropy, can be extrapolated from those of the other actinide hexahalides (Kim and Mulford, 1990). Its enthalpy of formation is derived from the extrapolation of the mean bond enthalpy of the other actinide hexahalides, which linearly varies along the actinide series.

Except for UCl_6, no other gaseous hexachlorides are known. The molecular properties of UCl_6 have not been determined experimentally. Estimates (Hildenbrand *et al.*, 1985) have been used in the NEA assessments (Grenthe *et al.*, 1992; Guillaumont *et al.*, 2003) but more recently reliable results from quantum chemical calculations have become available (Han, 2001). An approximate value for the enthalpy of formation of UCl_6 is derived from vapor pressure measurements performed in the 1940s (see Grenthe *et al.* (1992)).

19.6.2 Pentahalides

(a) Solid pentahalides

Fuger *et al.* (1983) accepted the enthalpies of formation of $PaCl_5$, $PaBr_5$, and α-UF_5 and β-UF_5 (as well as some intermediate uranium fluorides) to be well established based upon single reliable thermochemical studies by Fuger and Brown (1975) for the Pa compounds, and by O'Hare *et al.* (1982) for the UF_5 modifications. For UCl_5, Fuger *et al.* (1983) discussed the results of three different studies, but these gave an unclear picture. The discrepancy seems to be resolved by the measurements of Cordfunke *et al.* (1982). Properties of UBr_5 are based on high-temperature heterogeneous equilibria and have large uncertainties when extrapolated to 298.15 K. The other pentahalides (PaF_5, NpF_5) have not been studied thermochemically. The properties of PaF_5 cannot yet be estimated because of insufficient experimental data. Those of NpF_5 have been approximated by Lemire *et al.* (2001) on the basis of the experimental observation that NpF_5 does not disproportionate to NpF_6(g) and NpF_4(cr) below 591 K (Malm *et al.*, 1993).

The experimental basis for the entropies of the actinide pentahalides is very poor. Low-temperature heat capacity measurements have only been reported for UF_5 (Brickwedde *et al.*, 1951), but the sample contained 17% UF_4 and UO_2F_2. Fuger *et al.* (1983) adjusted the result for $S°(298.15\ K)$ by $+11.3\ J\ K^{-1}\ mol^{-1}$, to be consistent with dissociation pressure measurements in the U–F system. Fuger *et al.* also gave (rough) estimates of the entropies of $PaCl_5$, $PaBr_5$, and UCl_5, based on a systematic difference between MX_4 and MX_5 compounds.

Table 19.16 *High-temperature heat capacity of the actinide halides;* $C_p/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a(\mathrm{T/K})^{-2} + b + c(\mathrm{T/K}) + c(\mathrm{T/K})^2$ *(estimated values in italics);* $T_{\mathrm{min}} = 298.15$ K; T_{trs} *and* $\Delta_{\mathrm{trs}}H$ *refer to transition or fusion, as can be deduced from the phase indicators.*

		a ($\times 10^6$)	b	c ($\times 10^3$)	T_{trs} (K)	$\Delta_{\mathrm{trs}}H$ (kJ mol^{-1})	*References*
UF_6	cr		52.318	383.798	337.20	19.196	a
	l	–2.87646	215.338	1.9962			a
NpF_6	cr		62.333	352.547	327.91	17.520	a
	l		150.344	110.076			a
PuF_6	cr		168.1		*317*	*17.0*	a
UCl_6	cr	–0.7406	173.427	35.0619	*452*	*20.9*	b
	l		214				b
UF_5	β	–0.1926	125.478	30.2085	398		a
UF_5	α	–0.1926	125.478	30.2085	621		a
$PaCl_5$	cr				579	31.5	b
UCl_5	cr		140.164	35.564	*600*	*35.6*	a
$PaBr_5$	cr				556	35.4	b
ThF_4	cr	–1.255	122.173	8.37	1383	*41.8*	b
	l		*133.9*				b
UF_4	cr	–0.41316	114.5194	20.5549	1309	44.79	c
	l		174.0				c
NpF_4	cr	–0.83646	122.635	9.684	*1305*	*47*	a
PuF_4	cr	–1.091	127.53	3.114	*1300*	*47*	a
$ThCl_4$	cr	*–0.615*	*120.290*	*23.267*	1043	61.5	b
	l		*167.4*				b
$PaCl_4$	cr				*950*		b
UCl_4	cr	–0.0900	106.859	48.6448	863	49.8	a
	l		162.34				a
$NpCl_4$	cr	*–0.11*	*112.5*	*36*	*811*	*59.6*	a

$ThBr_4$	β	*–0.62*	*127.6*	*15.1*	952	*54.4*	c
	l		171.5				c
UBr_4	cr		119.244	29.7064	791	36 ± 5	a
	l		*172*				b
$NpBr_4$	cr		119	30	*800*	*50*	a
ThI_4	cr	*–0.6067*	*129.7*	*12.97*	843	*48*	b
	l		176				b
UI_4	cr	–1.97485	145.603	9.9579	*779*	*38*	a,b
	l		165.7				b
UF_3	cr	–1.0355	106.541	0.70542	1768	36.8	a
NpF_3	cr	–1.0	105.2	0.812	*1735*	*36.1*	a
PuF_3	cr	–1.0355	104.078	0.707	1700	*35.4*	a
AmF_3	cr				1666 ± 20		e
CmF_3	cr				1679 ± 20		e
UCl_3	cr	0.4583	87.78	31.120	1115	49.0	a
$NpCl_3$	cr	0.36	89.6	27.5	*1075*	*50*	a
$PuCl_3$	cr	0.24	91.35	24	1041	55	a
$AmCl_3$	cr				990 ± 5	48.1 ± 0.4	d,e,f
$CmCl_3$	cr				997 ± 5	47.9 ± 0.4	d,e
UBr_3	cr		97.971	26.360	1003	43.9	a
$NpBr_3$	cr	–0.32	101.23	20.68	*975*	*48*	a
$PuBr_3$	cr	–0.638	104.5	15.0	935	47.1	a
UI_3	cr		105.018	24.2672	*800*		a

[a] NEA-TBD (Grenthe *et al*., 1992; Lemire *et al*., 2001; Guillaumont *et al*., 2003).
[b] Fuger *et al*. (1983).
[c] Rand (1975).
[d] Burnett (1966).
[e] Weigel and Kohl (1985).
[f] Peterson and Burns (1973).

Their value for $PaCl_5$ is, however, significantly lower than that derived by Kovács *et al.* (2003) by combining the entropy of sublimation from the work of Weigel *et al.* (1969) with the entropy of the gas obtained from quantum chemical data. A comparison to other MCl_5 compounds showed that this value for solid $PaCl_5$ is unexpectedly high compared to UCl_5 and the transition metal pentahalides, which Kovács *et al.* attributed to the distinctly different crystal structure of $PaCl_5$ (pentagonal bipyramidal). However, no calorimetric measurements have been performed for any of the pentachloride compounds, and all entropies have been derived from (other complex) solid–gas equilibria.

The selected solid pentahalide data are listed in Table 19.15.

(b) Gaseous pentahalides

$PaCl_5$, $PaBr_5$, UF_5, UCl_5, UBr_5, and PuF_5 are the only gaseous pentahalides that have been studied experimentally. Vapor pressure measurements for the protactinium pentahalides were reported by Weigel *et al.* (1969, 1974) from which the enthalpy of formation of $PaCl_5$ has been derived (see Table 19.17). The interpretation of the UF_5 vapor pressure measurements is complicated due to the existence of dimeric molecules and dissociation reactions. The enthalpy of formation of UF_5 can also be derived from molecular equilibrium measurements by mass spectrometry. At least six such studies have been performed. They were reviewed in the NEA-TDB (Grenthe *et al.*, 1992; Guillaumont *et al.*, 2003) and the recommended values from that work are included in Table 19.17. Also for $UCl_5(g)$ and $UBr_5(g)$, molecular equilibrium studies have been performed. The derived enthalpies of formation are included in Table 19.17. An approximate value for the enthalpy of formation of PuF_5 was calculated indirectly from ionization potential measurements by Kleinschmidt (1988), but since this value is rather uncertain, it is not included.

Table 19.17 *Thermodynamic properties of the gaseous hexa- and pentahalides; estimated values are given in italics.*

	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
UF_6	376.3 ± 1.0	–2148.6 ± 1.9	[a]
UCl_6	438.0 ± 5.0	–985.5 ± 5	[a]
NpF_6	376.643 ± 0.500	–1921.66 ± 20.00	[a]
PuF_6	368.90 ± 1.00	–1812.7 ± 20.1	[a]
AmF_6	399.0 ± 5.0	*–1606 ± 30*	[a]
PaF_5	385.6	–2130 ± 50	[b]
$PaCl_5$	440.8	–1042 ± 15	[b]
UF_5	386.4 ± 10.0	–1913 ± 15	[a]
UCl_5	438.7 ± 5.0	– 900 ± 15	[a]
UBr_5	498.7 ± 5.0	–648 ± 15	[a]

[a] NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[b] Kovács *et al.* (2003).

Little experimental information exists on the molecular properties of the actinide pentahalides. Spectroscopic experiments of matrix-isolated UF_5 molecules (Kunze *et al.*, 1976; Paine *et al.*, 1976; Jones and Ekberg, 1977) indicate a tetragonal pyramidal structure (C_{4v}). Quantum chemical calculations (Wadt and Hay, 1979; Onoe *et al.*, 1997) showed that energy barrier between the C_{4v} and the trigonal bipyramidal structure (D_{3h}) is small (<4 kJ mol^{-1}) and it was suggested that the structure of UF_5 may be fluxional between C_{4v} and D_{3h} at high temperatures. Quantum chemical calculations of PaF_5 and $PaCl_5$ gave similar results (Kovács *et al.*, 2003). The derived entropy values are included in Table 19.17. It is likely that the Pa compounds follow the trend in the d-transition metal halides and have a D_{3h} equilibrium structure, whereas the U pentahalides have a C_{4v} equilibrium structure as a result of stronger participation of the 5f electrons in the An–F bonding.

19.6.3 Tetrahalides

(a) Solid tetrahalides

(i) Enthalpy of formation

Knowledge of actinide tetrafluoride enthalpies of formation is relatively poor. UF_4 has been studied extensively but the review by Grenthe *et al.* (1992) lists 14 experimental studies that show considerable scatter. Their selected value is based on reliable thermochemical cycles with UF_6(cr) using fluorine combustion calorimetry (Johnson, 1985) and UO_3(cr) using solution calorimetry (Cordfunke and Ouweltjes, 1981), which yielded values that differ by 10.7 kJ mol^{-1}. For ThF_4 the values derived from combustion calorimetry and high-temperature equilibria are discordant, as was discussed in detail by Wagman *et al.* (1977). We adopt here the value recommended by these authors, with increased uncertainty limits. For PuF_4, there are only estimates from the high-temperature equilibria, as discussed in detail by Lemire *et al.* (2001). Estimates of the enthalpies of formation of AmF_4 and CmF_4 can be derived from decomposition measurements by Gibson and Haire (1988a,b). We have accepted the assessed values for UF_4, NpF_4, and PuF_4 of the NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001) and made estimates of tetrafluoride thermochemistry with those of other tetravalent compounds.

The situation for the other tetrahalides is globally better. The most reliable values for UCl_4 of the ten studies performed cluster around -1019 kJ mol^{-1} (Grenthe *et al.*, 1992). Also the enthalpies of formation of thorium, protactinium, uranium, and neptunium tetrahalides appear to be well established. For the thorium and protactinium compounds, we have accepted the recommended values by Fuger *et al.* (1983) for the uranium, neptunium, plutonium, and americium compounds as the recommended values of NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003). Table 19.18

Table 19.18 *Thermodynamic properties of crystalline actinide(IV) halides at* 298.15 K (*estimated values in italics*); *see text for references.*

	AnF_4(cr)		$AnCl_4$(cr)		$AnBr_4$(cr)		AnI_4(cr)	
An	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})
Th	142.05 ± 0.21	–2097.9 ± 8.4	*183.5 ± 5*	–1186.2 ± 1.7	*227 ± 5*	–964.4 ± 2.1[a]	*251 ± 5*	–670.7 ± 2.1
Pa	*153 ± 3*	*–1946*	*196 ± 5*	–1046.3 ± 14.3	*238 ± 5*	–828.4 ± 14.3	*262 ± 5*	–525.2 ± 16.6
U	151.7 ± 0.2	–1914.2 ± 4.2	197.2 ± 0.8	–1018.8 ± 2.5	*240 ± 5*	–802.1 ± 2.5	*264 ± 5*	–518.3 ± 2.8
Np	*148 ± 3*	*–1874 ± 16*	*196 ± 5*	–984.0 ± 1.8	*233 ± 5*	–771.2 ± 1.8		
Pu	147.25 ± 0.37	*–1850 ± 20*	*195 ± 5*[b]	*–968.7 ± 5.0*[b]				
Am	*149 ± 5*	*–1724 ± 17*						
Cm	*135 ± 5*	*–1689*						
Bk		*–1793*						
Cf		*–1623*						
Es		*–1521*[b]						

[a] Beta modification.
[b] Believed to be unstable.

lists and Fig. 19.21 plots the enthalpies of formation of all known tetravalent actinide compounds and the aqueous ions as a function of Z. The enthalpy scale has been compressed to facilitate comparison. Interpolations can be made, using the best-fit curves shown, because each set of tetravalent compounds is isostructural, and other enthalpies of formation have thereby been estimated. The differences between the values thus calculated and those predicted by Fuger *et al.* (1983) are relatively small.

An interesting but unstable compound is $PuCl_4$. It has been detected in the gas phase by Gruen and DeKock (1967). Abraham *et al.* (1949) observed an increased volatility of $PuCl_3$ in a stream of chlorine gas. This was explained by the formation of gaseous $PuCl_4$, which decomposed to form solid $PuCl_3$ and Cl_2 upon condensation. Nevertheless, by comparison with other tetrahalides and complex chlorides, the enthalpy of formation of $PuCl_4$(s) is predictable within narrow error limits and has been included in Table 19.18 and Fig. 19.21.

(*ii*) *Heat capacity and entropy*

The low-temperature heat capacities of ThF_4, UF_4, PuF_4, and UCl_4 have been measured experimentally. The results for the fluorides are reliable. The measurements for UF_4 have been made down to 1.3 K and include careful analysis of the excess entropy contribution arising from the Schottky anomaly that corresponds to a crystal field level of 10.7 cm^{-1} for the U^{4+} ions at the C_2 symmetry site (one-third of the ions). The heat capacity measurements for UCl_4 (15–355 K) date from the World War II period and have only been reported in summary in the *Chemistry of Uranium* by Katz and Rabinowitch (1951). The recommended entropies of these actinide tetrahalides are listed in Table 19.18. We have estimated the entropies of the other tetrafluorides and tetrachlorides from these values using equations (19.10) and (19.11), and the procedure described for the dioxides.

The values for the tetrabromides and tetraiodides are estimates based on extrapolation of the trend F to I. It is known from transition metal and lanthanide halides that the entropies regularly increase as a function of the logarithm of the halide mass. Fig. 19.22 shows the relationship between the entropy divided by the number of halide ligands (n) for the uranium and europium halides. We have extrapolated the almost parallel relations as indicated, and used the estimated values for the UBr_4 and UI_4 as a basis for the estimation.

(*iii*) *High-temperature properties*

High-temperature data for the actinide tetrahalides are even more problematic. Experimental enthalpy increment data have been measured for UF_4 and ThF_4 crystal, but the results of ThF_4 are unpublished (see Fuger *et al.* (1983) and references therein). No high-temperature data for the tetrabromides have been

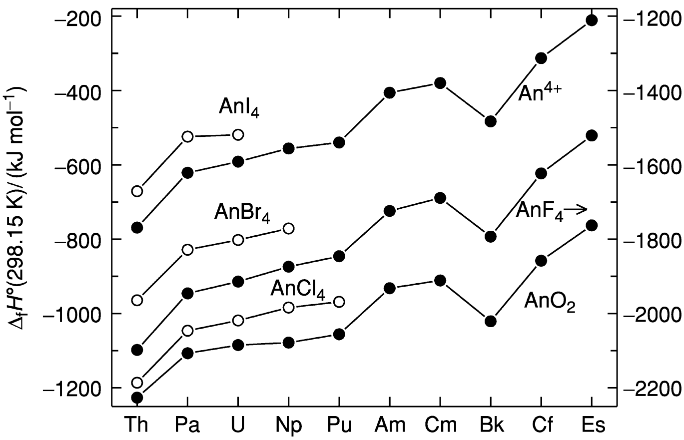

Fig. 19.21 *Comparison of enthalpies of formation of actinide*(IV) *species.*

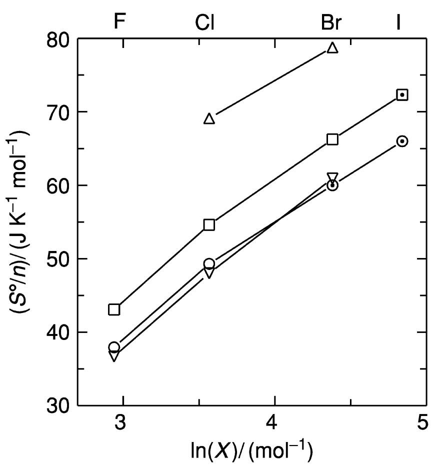

Fig. 19.22 *The relation between the entropy divided by the number of halide ligands n and the logarithm of the halide mass* (X), *for the uranium and europium halides;* □, UX_3, ○, UX_4, Δ, UOX_2, ∇, EuX_3. *Estimated values are indicated by dotted symbols.*

reported, but a heat capacity study of UI_4 was made by Popov *et al.* (1959). This study indicated a phase transition close to the melting point. From these data the heat capacity of the other actinide tetrahalides were estimated with reasonable accuracy by Fuger *et al.* (1983) and later by the NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003). The values thus obtained are listed in Table 19.16.

(b) Gaseous tetrahalides

The gaseous tetrahalides of uranium have been the subject of studies for many years. Early electron diffraction studies were interpreted as a tetrahedral (T_d) structure whereas later measurements on UX_4 molecules seem to indicate a distorted tetrahedron. The latter seemed to be confirmed by analyses of vapor pressure data (Hildenbrand, 1988), which gave good second/third law agreement in case a C_{2v} molecular structure was assumed. Only in the 1990s it was established with certainty by a combination of gas-phase electron diffraction, high-temperature gas-phase infrared spectroscopy, and quantum chemical calculations that UF_4 and UCl_4 have a tetrahedral structure (Haaland *et al.*, 1995; Konings *et al.*, 1996). The entropies of UF_4 and UCl_4 calculated from the molecular and vibrational parameters derived from these studies are consistent with the entropies obtained from vapor pressure measurements, which have been reported for most of these compounds. Konings and Hildenbrand (1998) discussed in detail that this is essentially true for all known gaseous actinide tetrahalides, for which they estimated the molecular and vibrational parameters in a systematic manner. Since then further electron diffraction results and also results from quantum chemical calculations have become available, which have led to further refinement of the recommended values.

The calculated entropies and the enthalpies of formation derived from vapor pressure measurements for these species are listed in Table 19.19. The numbers principally come from the NEA-TDB reviews, in which the most recent refinements have not been included and a simplified approach to the estimation of the vibrational frequencies was used. However, since this will have a moderate effect, we have accepted these numbers.

19.6.4 Trihalides

(a) Solid trihalides

(*i*) *Enthalpy of formation*

Trigonal trifluorides are known for all the actinides Ac and U–Cf. Surprisingly, thermodynamic measurements have been performed only for UF_3 and PuF_3; even more surprising is the unsatisfactory situation regarding even these two trifluorides. Fuger *et al.* (1983) and later Grenthe *et al.* (1992) have evaluated all of the experimental results and listed their unresolved questions. For UF_3 several independent thermochemical pathways have been used, yielding unresolvable inconsistencies with a variety of uranium species; sample impurities plagued the fluorine combustion measurements and complex thermochemical cycles, involving many species, obfuscate the solution calorimetry measurements. For PuF_3 the one measurement (Westrum and Eyring, 1949) is uncertain primarily because it was a reaction to an unanalyzed trifluoride precipitate assumed to be anhydrous but probably $PuF_3 \cdot 0.4H_2O$. Nevertheless,

Table 19.19 *Thermodynamic properties of the gaseous tetra- and trihalides; estimated values are in italics.*

Molecule	$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*
ThF_4	351.6 ± 3.0	–1748.2 ± 8.4	a
$ThCl_4$	398.5 ± 3.0	–953.4 ± 1.8	a
$ThBr_4$	443.6 ± 3.0	–746.3 ± 2.3	a
ThI_4	503.8 ± 5.0	–436.9 ± 2.3	a
UF_4	360.7 ± 5.0	–1605.2 ± 6.5	b
UCl_4	409.3 ± 5.0	–815.4 ± 4.7	b
UBr_4	451.9 ± 5.0	–605.6 ± 4.7	b
UI_4	499.1 ± 8.0	–305.0 ± 5.7	b
NpF_4	369.8 ± 10.0	–1561 ± 22	b
$NpCl_4$	423.0 ± 10.0	–787.0 ± 4.6	b
PuF_4	359.0 ± 10.0	–1548 ± 22	b
$PuCl_4$	409.0 ± 10.0	–792.0 ± 10.0	b
UF_3	347.5 ± 10.0	–1065 ± 20	b
UCl_3	380.3 ± 10.0	–523 ± 20	b
UBr_3	403 ± 15	–371 ± 20	b
UI_3	431.2 ± 10.0	–137 ± 25	b
PuI_3	*435 ± 15*	*– 305 ± 15*	b
NpF_3	330.5 ± 5.0	–1115 ± 25	b
$NpCl_3$	362.8 ± 10.0	–589.0 ± 10.4	b
PuF_3	336.1 ± 10.0	–1167.8 ± 6.2	b
$PuCl_3$	368.6 ± 10.0	–647.4 ± 4.0	b
$PuBr_3$	423 ± 15	–488 ± 15	b
AmF_3	330.4 ± 8.0	–1156.5 ± 16.6	b

[a] Recalculated in this study.
[b] NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

these two data points must be used to compare and to predict the properties of all f-element trifluorides.

Fortunately, there are enthalpy-of-formation data on almost all lanthanide trifluorides, though not all of them are reliable (Konings and Kovács, 2003). Table 19.20 and Fig. 19.23 present these data along with structural data that permit a correlation of the quantity $\{\Delta_f H°(MF_3,cr) - \Delta_f H°(M^{3+},aq)\}$ with the ionic radii. It can be seen that the most reliable data for the lanthanide trifluorides fall into two groups of different crystal structures (trigonal/hexagonal and orthorhombic), and that the two actinide trifluorides (trigonal) do not clearly fit to this trend. Clearly, the correlation is less evident than for the lanthanide chlorides, bromides, and iodides so that the correlation will have limited value until better lanthanide and actinide trifluoride enthalpy measurements are made.

Trichlorides, tribromides, and triiodides of all elements from uranium through einsteinium are known. Solution calorimetry enthalpies of formation

Table 19.20 *Enthalpies of formation and entropies of the crystalline lanthanide and actinide trifluorides; estimated values are in italics.*

	S°(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$(298.15 K) ($kJ\ mol^{-1}$)	*References*		S°(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$(298.15 K) ($kJ\ mol^{-1}$)	*References*
AcF_3	*115.8 ± 4.0*	*–1670 ± 40*		LaF_3	106.98 ± 0.11	–1699 ± 2	d
				CeF_3	*119.7*	–1703	d
				PrF_3	121.22 ± 0.12	–1689 ± 3	d
UF_3	129.22 ± 0.5	–1501.4 ± 4.7	a,b	NdF_3	120.79 ± 0.12	–1679 ± 2	d
NpF_3	*130.6 ± 3.0*	*–1529 ± 8*	a,b	PmF_3	*120.6*	*–1668*	d
PuF_3	126.11 ± 0.36	–1586.7 ± 3.7	a,b	SmF_3	*116.5*	–1669 ± 5	d
AmF_3	*110.6 ± 3.0*	*–1594 ± 14*	a,b	EuF_3	*110.1*	–1571	d
CmF_3	*127.0 ± 3.0*	*–1599 ± 35*	a	GdF_3	114.77 ± 0.22	–1699 ± 2	d
BkF_3	*130.0 ± 5.0*	*–1581 ± 35*	c	TbF_3	*119.9*	–1707	d
CfF_3	*131.0 ± 5.0*	*–1553 ± 35*	c	DyF_3	119.07 ± 0.12	–1692 ± 2	d
EsF_3		*–1575 ± 40*	c	HoF_3	*120.3*	–1698 ± 2	d
				ErF_3	116.86 ± 0.12	–1694 ± 2	d
				TmF_3	*115.0*	–1656	d
				YbF_3	*111.8*	–1570	d
				LuF_3	116.86 ± 0.12	–1701	d

[a] Konings (2001a).
[b] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[c] Estimated in present work.
[d] Konings and Kovács (2003).

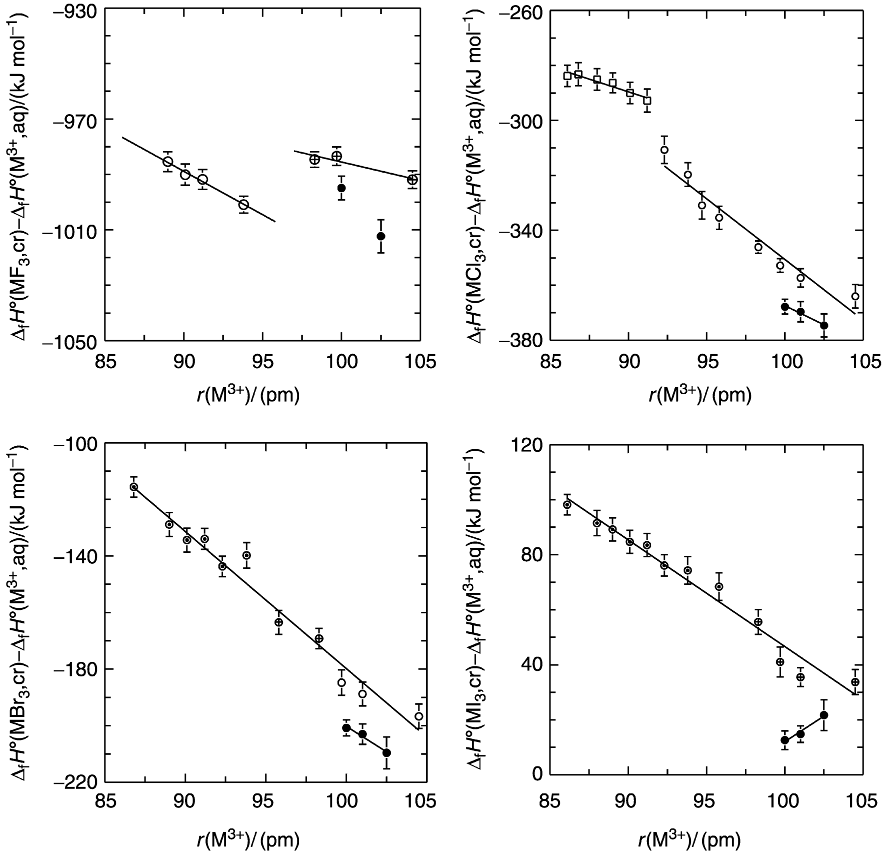

Fig. 19.23 *The difference between the enthalpies of formation of f-element trihalides* (*at* 298.15 K) *and the corresponding M^{3+} aqueous ions; the lanthanides are shown by open symbols that indicate the different crystallographic structures; the actinides are shown by closed symbols.*

are known for these trihalides of uranium through plutonium, although that of $NpCl_3$ requires an estimate of its heat of solution (Fuger *et al.*, 1983). In addition, the enthalpies of formation of $AmCl_3$ and $CfBr_3$ are known from solution calorimetry; that of other actinide trihalides as well as heavier trihalides must be estimated. This can be done by a correlation of the quantity $\{\Delta_f H°(MX_3,cr) - \Delta_f H°(M^{3+},aq)\}$ with ionic radius for isostructural compounds (Fig. 19.23). It can be seen that the trend in the actinide chloride and bromides series is parallel to that in the lanthanide series and thus permits extrapolation beyond Pu. In the actinide iodides, the trend is opposite. Such data sets are shown in Tables 19.21–19.23. The resultant enthalpies of formation are consistent with the data reported in the NEA-TDB project.

Table 19.21 *Enthalpies of formation and entropies of the crystalline lanthanide and actinide trichlorides; estimated values are in italics.*

	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*		$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
$AcCl_3$	*148.7 ± 6.0*	*–1053*	a	$LaCl_3$	137.57	–1071.6 ± 1.5	d
				$CeCl_3$	*151.0*	–1059.7 ± 1.5	d
				$PrCl_3$	153.30	–1058.6 ± 1.5	d
UCl_3	163.90 ± 0.50	–863.7 ± 2.0	b,c	$NdCl_3$	153.43	–1040.9 ± 1.0	d
$NpCl_3$	*165.2 ± 6.0*	–896.8 ± 3.0	b,c	$PmCl_3$	*153.3*	*–1030 ± 10*	d
$PuCl_3$	*161.4 ± 6.0*	–959.6 ± 1.8	b,c	$SmCl_3$	150.12	–1025.3 ± 2.0	d
$AmCl_3$	*146.2 ± 6.0*	–977.8 ± 1.3	b,c	$EuCl_3$	144.06	–935.4 ± 3.0	d
$CmCl_3$	*163.1 ± 6.0*	–969.6 ± 6.7	a	$GdCl_3$	151.42	–1019.2 ± 1.5	d
$BkCl_3$	*164.6 ± 6.0*	*–952 ± 15*	a	$TbCl_3$	*176.7*	–1010.6 ± 3.0	d
$CfCl_3$	*167.2 ± 6.0*	*–965 ± 20*	a	$DyCl_3$	175.4	–993.1 ± 3.0	d
$EsCl_3$		*–950 ± 24*	a	$HoCl_3$	177.1	–997.7 ± 2.5	d
$FmCl_3$		*–963 ± 44*	a	$ErCl_3$	175.1	–994.4 ± 2.0	d
$MdCl_3$		*–864 ± 50*	a	$TmCl_3$	173.5	–996.3 ± 2.5	d
$NoCl_3$		*–716 ± 50*	a	$YbCl_3$	169.3	–959.5 ± 3.0	d
				$LuCl_3$	153.0	–987.1 ± 2.5	d
$PuCl_3 \cdot 6H_2O$	*420 ± 5*	–2773.4 ± 2.1	b				

[a] Estimated in the present work.
[b] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001).
[c] Konings (2001a).
[d] Konings and Kovács (2003).

Table 19.22 *Enthalpies of formation and entropies of the crystalline lanthanide and actinide tribromides; estimated values are in italics.*

	S°(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$(298.15 K) ($kJ\ mol^{-1}$)	*References*		S°(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$(298.15 K) ($kJ\ mol^{-1}$)	*References*
$AcBr_3$	*164 ± 6*	*–896 ± 30*	a	$LaBr_3$	*177.1*	–904.4 ± 1.5	d
				$CeBr_3$	*191.2*	–891.2 ± 1.5	d
				$PrBr_3$	*193.8*	–890.5 ± 4.0	d
UBr_3	198.74 ± 0.40	–698.7 ± 4.2	b	$NdBr_3$	*193.6*	–864.0 ± 3.0	d
$NpBr_3$	*200 ± 6*	–730.2 ± 2.9	b	$PmBr_3$	*192.6*	*–858 ± 10*	d
$PuBr_3$	*196 ± 6*	–792.6 ± 2.0	b	$SmBr_3$	*189.4*	–853.4 ± 3.0	d
$AmBr_3$	*181 ± 6*	*–804.0 ± 6.0*	b	$EuBr_3$	182.8	*–759 ± 10*	d
$CmBr_3$	*198 ± 6*	*–800.3 ± 7.0*	c	$GdBr_3$	*209.0*	–838.2 ± 2.0	d
$BkBr_3$	*199 ± 6*	*–781.5 ± 6.5*	c	$TbBr_3$	*212.3*	–843.5 ± 3.0	d
$CfBr_3$	*202 ± 6*	–752.5 ± 3.2	c	$DyBr_3$	*213.4*	–834.3 ± 2.5	d
				$HoBr_3$	*213.1*	–842.1 ± 3.0	d
				$ErBr_3$	*212.2*	–837.1 ± 3.0	d
				$TmBr_3$	*210.2*	*–832 ± 10*	d
				$YbBr_3$	*204.8*	–791.9 ± 2.0	d
				$LuBr_3$	*188.7*	–814 ± 10	d

[a] Estimated in present work.
[b] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[c] Fuger *et al.* (1990).
[d] Konings and Kovács (2003).

Table 19.23 *Enthalpies of formation and entropies of the crystalline lanthanide and actinide triiodides; estimated values are in parentheses.*

	$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*		$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*
				LaI_3	*196.3*	–673.9 ± 2.0	c
				CeI_3	*210.4*	–666.8 ± 3.0	c
				PrI_3	*213.0*	–664.7 ± 5.0	c
UI_3	*217 ± 5*	–466.9 ± 4.2	a	NdI_3	*212.8*	–639.2 ± 4.0	c
NpI_3	*218 ± 5*	–512.4 ± 2.2	b	PmI_3	*230.6*	*–634 ± 10*	c
PuI_3	*214 ± 5*	–579.2 ± 2.8	b	SmI_3	*227.4*	–621.5 ± 4.0	c
AmI_3	*199 ± 3*	*–615 ± 9*	b	EuI_3	*220.8*	*–538 ± 10*	c
				GdI_3	*220.8*	–624.1 ± 3.0	c
				TbI_3	*228.2*	–623.8 ± 3.0	c
				DyI_3	*231.5*	–616.7 ± 3.0	c
				HoI_3	*232.5*	–622.9 ± 3.0	c
				ErI_3	*232.3*	–619.0 ± 3.0	c
				TmI_3	*228.7*	–619.7 ± 3.5	c
				YbI_3	*223.1*	*–578 ± 10*	c
				LuI_3	206.7	–605.1 ± 2.2	c

[a] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[b] Estimated in the present work.
[c] Konings and Kovács (2003).

(*ii*) *Heat capacity and entropy*

Low-temperature heat capacities of UF_3 and PuF_3 have been measured, and high-temperature data are only available for UF_3. Recently, an inconsistency between the low-temperature data for these compounds was pointed out by Konings (2001a). The entropy value of PuF_3, derived from measurements by Osborne *et al.* (1974), yields a lattice entropy that is significantly higher than that of UF_3 derived from data by Cordfunke and Westrum, which are only published as a summary (Cordfunke *et al.*, 1989). This lattice entropy is not consistent with those of the lanthanide trifluorides and it was suggested that the extrapolation to 0 K of the UF_3 value did not include the magnetic contribution, which is equal to $R \ln(2)$ and completely removes the inconsistency. From the results for PuF_3 and those for the lanthanide trifluorides, Konings (2001a) estimated the lattice entropies of NpF_3, AmF_3, and CmF_3 which were combined with an excess entropy calculated from crystal field levels to give the standard entropy. These values are given in Table 19.20.

Heat capacity and thus entropy data for the other actinide trihalides have only been reported for UCl_3 and UBr_3. As discussed above the entropy values for UCl_3 and UBr_3 derived from the results of Cordfunke *et al.* (1989) must be $R \ln(2)$ higher to account for the magnetic contribution at low temperatures (Konings, 2001a). Estimates for the standard entropies of the transuranium trichlorides up to $CmCl_3$ were presented by Konings (2001a) and are included in Table 19.21. Estimates for the standard entropy for the uranium triiodide and the bromides and iodides of neptunium, plutonium, and americium were presented in the NEA-TDB project, but the method used is less accurate than that proposed by Konings (2001a). In the case of the americium compounds, where the differences between the two sets of data largely exceeds the uncertainty limits, the values proposed by Konings (2001a) have been adopted by the NEA-TDB project (Guillaumont *et al.*, 2003). The value for $PuCl_3 \cdot 6H_2O$ is included in Table 19.21 as it is a key value for the estimation of the entropies of the aqueous ion of this element.

(*iii*) *High-temperature properties*

The high-temperature heat capacity of solid UF_3, UCl_3, and UBr_3 has been derived from enthalpy increment measurements (Cordfunke *et al.*, 1989). Measurements for other actinide trihalides have not been made. As discussed by Konings and Kovács (2003) the heat capacity of the lanthanide trihalides can be described very well as the sum of the lattice and excess components, the latter arising from the electronic states of the lanthanide ions. A similar approach can be used for the estimation of the heat capacity of the actinide trihalides. The recommended functions are listed in Table 19.16.

The melting point and melting enthalpy of many trihalides have been reported. They are summarized in Table 19.16. The data for the trichlorides

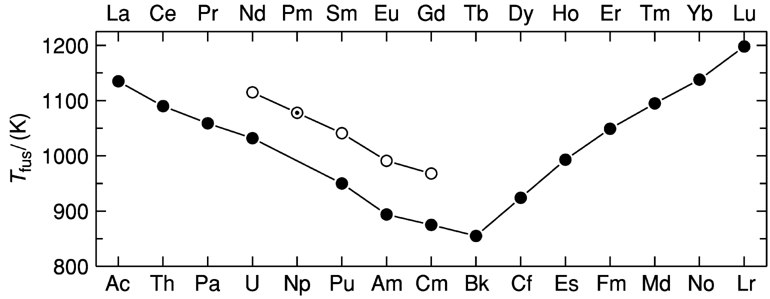

Fig. 19.24 *Melting temperature of the lanthanide* (•) *and actinide* (○) *trichlorides; estimated values are indicated by* (⊙).

are the most extensive; they are known from UCl_3 to $CmCl_3$. These values are of the same order as those of the lanthanide trichlorides and the trend in the actinide trichlorides series is parallel, as shown in Fig. 19.24.

(b) Gaseous trihalides

The situation for the gaseous actinide trihalides is complicated: the measured condensed gas-phase equilibria are not always clearly defined, the condensed phase data are often uncertain (see above) and the molecular geometry of these species has not been measured except for UCl_3 and UI_3. For these two compounds, gas-phase electron diffraction (ED) measurements have been reported (Bazhanov *et al.*, 1990a,b), which indicated a pyramidal structure with a X–M–X bond angle close to 90°. Quantum chemical calculations for the uranium(III) halides also indicate a pyramidal structure (Joubert and Maldivi, 2001) but with a bond angle much closer to the planar 120°. Fortunately, the molecular properties of the lanthanide trihalides are much better known and can be used for comparison. Experimental and theoretical studies have indicated a gradual increase of the X–Ln–X bond angle to the planar 120° from F to I and La to Lu (Molnar and Hargittai, 1995; Konings and Kovács, 2003), which is consistent with simple steric considerations. The lanthanide trifluorides are most probably pyramidal, the trichlorides, tribromides, and triiodides are quasi-planar (light lanthanides) or planar (heavy lanthanides). Quantum chemical calculations for UCl_3 and UI_3 agree with this trend but the experimental bond angles for UCl_3 $(95 \pm 3)°$ and UI_3 $(89 \pm 3)°$ disagree. The situation for the vibrational frequencies is equally complicated. The asymmetric stretching frequency of UCl_3 was determined experimentally by high-temperature infrared spectroscopic measurements (Kovács *et al.*, 1996), but the value (275 cm^{-1}) is considerably lower than those estimated from the electron diffraction data (310 ± 30 cm^{-1}) and derived from the quantum chemical calculations (300 cm^{-1} to 341 cm^{-1}, depending on the theoretical level). Clearly further research is needed to establish the molecular and thus the thermodynamic properties of the gaseous actinide trihalides more precisely. For the present chapter we accept the estimated values given in the NEA-TDB reviews, but increased the uncertainties assigned in that work. The values are given in Table 19.19.

Enthalpies of formation of gaseous UF_3, UCl_3, and UBr_3 have been evaluated from experimental studies by Grenthe *et al.* (1990) and the enthalpies of formation derived in this work are listed in Table 19.19. For UF_3, vapor pressure and molecular equilibria studies were used, and are in fair agreement. For UCl_3 and UBr_3, only the molecular equilibria studies were used. Such data are also available for the lower thorium fluorides, chlorides, and bromides. Vapor pressure measurements have been reported also for the trifluorides AmF_3, PuF_3, and CfF_3 and the trichlorides $PuCl_3$ and $AmCl_3$, and the tribromide $PuBr_3$.

Fig. 19.25 shows the mean bond enthalpy of the actinide trifluorides as well as of the lanthanide trifluorides. The figure shows approximately the same trend for the two groups, the actinide series being somewhat shifted compared to the lanthanide series. From this trend, the enthalpies of formation of the other gaseous trihalides can be estimated with confidence.

19.6.5 Di- and monohalides

(a) Solid dihalides

The existence of the dichlorides, dibromides, and diiodides of Am and Cf has been reported. However, no experimental thermochemical data are available. Because these dihalides parallel lanthanide dihalides of similar M^{2+} ionic radii, it is possible to estimate their enthalpies of formation by a method similar to that used by Morss and Fahey (1976), based on the difference $\{\Delta_f H°(MX_2,cr) - \Delta_f H°(M^{2+},aq)\}$. Konings (2002a) estimated the standard entropy of $AmCl_2$ as $S°(298.15\ K) = (148.1 \pm 5.0)\ J\ K^{-1}\ mol^{-1}$. This value is the sum of a lattice contribution estimated from the experimental data for some lanthanide

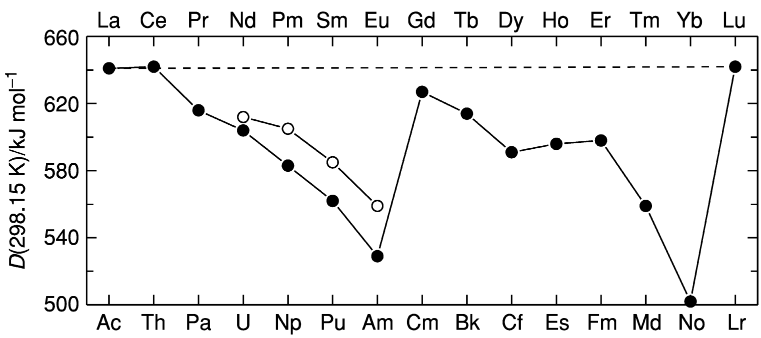

Fig. 19.25 *The mean bond enthalpy at* 298.15 K *of the gaseous lanthanide* (•) *and actinide trifluorides* (○).

dichlorides and the excess contribution R ln(8). Using a similar approach, we estimate the entropies of some other actinide dichlorides.

The data for these estimations, and the resulting predicted enthalpies of formation, are shown in Table 19.24. The Gibbs energies of these reactions are given in the following equations:

$$\mathrm{Am(cr)} + 2\mathrm{AmCl_3(cr)} = 3\mathrm{AmCl_2(cr)}, \quad \Delta_\mathrm{r}G = -35\ \mathrm{kJ\ mol^{-1}} \qquad (19.22)$$

and

$$\mathrm{Cf(cr)} + 2\mathrm{CfCl_3(cr)} = 3\mathrm{CfCl_2(cr)}, \quad \Delta_\mathrm{r}G = -91\ \mathrm{kJ\ mol^{-1}} \qquad (19.23)$$

illustrate the relative difficulty and ease of preparing the dihalides of americium compared to californium.

(b) Gaseous di- and monohalides

The di- and monohalides of thorium and uranium have been identified in mass spectrometric measurements by different authors. Lau and coworkers (Lau and Hildenbrand, 1982; Lau *et al.*, 1989) studied the exchange reactions of the lower thorium and uranium fluorides with BaF; Gorokhov *et al.* (1984) and Hildenbrand and Lau (1991) studied the molecular equilibria between the uranium fluorides among themselves. The results for the uranium compounds have been analyzed in detail by Grenthe *et al.* (1990) and updated by Guillaumont *et al.* (2003), who demonstrated that the results are in reasonable agreement, considering the large number of approximations made in the analysis. Similar studies have been made for the lower chlorides and bromides (Lau and Hildenbrand, 1984, 1987, 1990; Hildenbrand and Lau, 1990). Almost no experimental data on the molecular properties of these species are available and thus all thermal functions are based on rather qualitative estimates (using alkaline-earth dihalide data), introducing large uncertainties. For this reason, the recommended values for the lower uranium halide species given in Table 19.25 should be used with caution, especially when used well outside the temperature range of the experimental studies.

As discussed by Lau and Hildenbrand (1982), the mean bond energy decreases gradually in the uranium halide series (Fig. 19.26). This trend can be used to approximate the enthalpies of formation of the lower halides of other actinides, when needed.

19.7 COMPLEX HALIDES, OXYHALIDES, AND NITROHALIDES

19.7.1 Solid complex halides

Many complex halides of thorium and uranium have been prepared for crystallographic, magnetic, and spectroscopic studies. Preparative conditions suggested that these compounds are more stable than the parent (binary)

Table 19.24 *Enthalpies of formation and entropies of the crystalline lanthanide and actinide dichlorides; estimated values are in italics.*

	$S°(298.15\ K)$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°(298.15\ K)$ ($kJ\ mol^{-1}$)	*References*		$S°(298.15\ K)$ ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°(298.15\ K)$ ($kJ\ mol^{-1}$)	*References*
				$NdCl_2$	141.5	–707	a,b
				$PmCl_2$	*139.4*	–691	a,b
$PuCl_2$		*–528*	a	$SmCl_2$	132.2	–802	a,b
$AmCl_2$	*148.1*	*–654*	a,b	$EuCl_2$	138.5	–824	a,b
$CmCl_2$		*–516*	a				
$BkCl_2$		*–584*	a				
$CfCl_2$	*154*	*–669*	a	$DyCl_2$	141.7	–693	a,b
$EsCl_2$		*–694*	a				
$FmCl_2$		*–748*	a				
$MdCl_2$		*–752*	a	$TmCl_2$	137.4	–709	a,b
$NoCl_2$		*–763*	a	$YbCl_2$	120.0	–800	a,b

[a] Morss and Fahey (1976).
[b] Konings (2002a) and references therein.

Table 19.25 *Thermodynamic properties of the gaseous actinide di- and monohalides; estimated values are in italics from NEA-TDB* (*Grenthe* et al., 1992; *Guillaumont* et al., 2003).

	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})
UF_2	315.7 ± 10.0	–540 ± 25
UCl_2	339.1 ± 10.0	–155 ± 20
UBr_2	359.7 ± 10.0	–40 ± 15
UI_2	376.5 ± 10.0	103 ± 25
UF	251.8 ± 3.0	–47 ± 20
UCl	265.6 ± 3.0	187 ± 20
UBr	278.5 ± 3.0	245 ± 20
UI	286.5 ± 5.0	342 ± 20

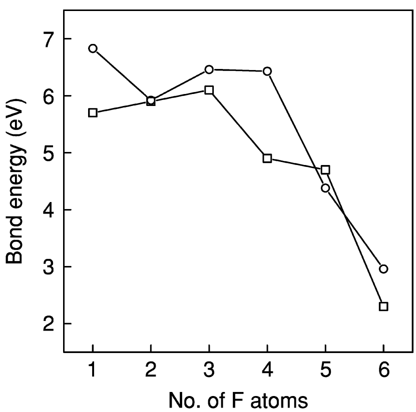

Fig. 19.26 *The bond dissociation energy of the $F_{n-1}AnF$ molecules as a function of n, the number of fluorine atoms in the molecule;* ○, *uranium fluorides;* □, *plutonium fluorides.*

halides. For example, UF_5 is difficult to prepare but complex halides such as $CsUF_6$ are relatively stable. Among the transuranium elements, fewer high-valent binary halides are known, but complex halides (e.g. Cs_2PuCl_6 and $CsPuF_6$) are known whereas the binary actinide halides ($PuCl_4$ and PuF_5) have been sought without success. Some of these complex halides have been exploited in separation schemes for the actinides. As discussed by Fuger *et al.* (1983), their thermodynamic properties have been of interest since the beginning of the 20th century.

Fuger *et al.* (1983) also assessed all of their thermodynamic properties. More recently the compounds of Np, Pu, and Am were also reviewed by the NEA-TDB teams (Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003). In Table 19.26 the values selected by the NEA teams are given for compounds of Np, Pu, and Am and the values selected by Fuger *et al.* (1983) for compounds of Th, Pa, and U. All these data have been recalculated using the latest NEA-selected values. In the framework of a general study on several $Cs_2NaAnCl_6$ compounds, Schoebrechts *et al.* (1989) also reported the enthalpy of formation of $Cs_2NaCfCl_6$ and estimates for the corresponding compounds of Cm and Bk. These values are also given in Table 19.26.

Fig. 19.27 displays the enthalpies of complexation, e.g.

$$2CsCl(cr) + UCl_4(cr) = Cs_2UCl_6(cr), \quad \Delta H = \Delta_{cplx}H \qquad (19.24)$$

of some of these compounds. Interpolation and extrapolation of $\Delta_{cplx}H$ along with enthalpies of formation of the binary compounds provide the values necessary to predict the enthalpies of formation of several of these complex halides. Note that $\Delta_{cplx}H$ becomes more favorable (exothermic) as the alkali-metal ion A^+ becomes larger and, to a lesser extent, as the actinide ion An^{4+} becomes smaller. As with complex oxides, these are both structural-packing (ionic) and acid–base (covalent) effects.

19.7.2 Solid oxyhalides and nitrohalides

There are many oxyhalides of actinide oxidation states +3 through +6. In general these are more stable than a mixture of oxide and halide, e.g.

$$UF_6(cr) + 2UO_3(c, \gamma) = 3UO_2F_2(cr), \quad \Delta_r G^\circ = -318 \text{ kJ mol}^{-1} \qquad (19.25)$$

reflecting the acid–base nature of the reactions. In some cases, however, e.g.

$$UCl_4(cr) + UO_2(cr) = 2UOCl_2(cr), \quad \Delta_r G^\circ = +12 \text{ kJ mol}^{-1} \qquad (19.26)$$

$$NpCl_4(cr) + NpO_2(cr) = 2NpOCl_2(cr), \quad \Delta_r G^\circ = +59 \text{ kJ mol}^{-1} \qquad (19.27)$$

the Gibbs energy of the reactions is positive, reflecting the limited stability of such oxyhalides with respect to the stoichiometric mixture of the oxide and chloride in the same oxidation state.

We have accepted the assessed enthalpies of formation from calorimetric and vapor–solid hydrolysis equilibria by Fuger *et al.* (1983) for Th, Pa, and Cm compounds, and the more recently assessed values by the NEA teams for compounds of U to Am (Table 19.27). Also included are the recent results of Burns *et al.* (1998) for CfOCl and BkOCl, the former based on experiments, the latter based on an interpolation in the AnOCl series (An = U, Pu, Am, Cm, and Cf).

Heat capacity data have been reported for uranium oxyhalides UO_2F_2, UO_2Cl_2, $UOCl_2$, and $UOBr_2$. The entropy values derived in these studies have been accepted in the NEA-TDB review (Grenthe *et al.*, 1992). High-temperature

Table 19.26 *Thermodynamic properties of crystalline actinide complex halides and oxyhalides with alkali metals; estimated values are in italics; see text for references.*

	S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)
			Na_3UF_7		–3672.0 ± 4.6	$NaUF_6$		–2694 ± 13[a]	$NaUF_7$	*272 ± 12*	–2804.9 ± 10.5
									Na_2UF_8	*330* ± 13	–3391.8 ± 12.6
									$Na_3UO_2F_5$		–3115.0 ± 2.5
									$Na(UO_2)_2F_5$		–3917.7 ± 2.9
						KUF_6		–2731.0 ± 5.0	$K_3UO_2F_5$		–3484.0 ± 2.5
									$K(UO_2)_2F_5$		–3954.9 ± 2.9
									$K_5(UO_2)_2F_9$		–6377.3 ± 6.6
			Rb_3UF_7		–3734.6 ± 3.3	$RbUF_6$		–2740.5 ± 5.9	$Rb_3UO_2F_5$		–3472.3 ± 3.3
									$Rb(UO_2)_2F_5$		–3964.8 ± 3.8
									$Rb_5(UO_2)_2F_9$		–6373.9 ± 7.5
			Cs_2UF_6		–3156.4 ± 4.2	$CsUF_6$		–2756.0 ± 5.4	$Cs_3UO_2F_5$		–3468.8 ± 6.3
									$Cs(UO_2)_2F_5$		–3977.8 ± 4.0
									$Cs_5(UO_2)_2F_9$		–6374.6 ± 10.3
			$LiThCl_5$		–1619.6 ± 4.2						
			Li_2ThCl_6		–2038.9 ± 6.3						
			Li_2UCl_6		–1831.3 ± 3.8						
			Na_2ThCl_6		–2041.4 ± 6.3						
			Na_2UCl_6		–1848.1 ± 2.1	$NaUCl_6$		–1472.3 ± 3.3[b]			
			K_2ThCl_6		–2110.8 ± 6.3						
			$KUCl_5$		–1481.1 ± 3.3						
			K_2UCl_6		–1931.8 ± 2.1	$KUCl_6$		–1525.5 ± 2.9			
			Rb_2ThCl_6		–2157.3 ± 6.3						
			Rb_4ThCl_8		–3063.5 ± 8.0						
			$RbUCl_5$		–1497.9 ± 4.2						
			Rb_2UCl_6		–1956.6 ± 3.6	$RbUCl_6$		–1553.5 ± 2.5			
			Rb_4UCl_8		–2828.7 ± 4.2						
			Cs_4ThCl_8		–3053.1 ± 8.0				$Cs_2UO_2Cl_4$		–2204.5 ± 2.5
			Cs_2ThCl_6		–2147.6 ± 2.1				$Cs_2NpO_2Cl_4$		–2056.1 ± 5.4
			Cs_2PaCl_6		–2030.8 ± 14.4[c]				$Cs_3NpO_2Cl_4$		–2449.1 ± 4.8

Table 19.26 (*Contd.*)

	S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)
Cs_2NaUCl_6		–2173.8 ± 4.1	CsU_2Cl_9		–2534.7 ± 7.7						
			$CsUCl_5$		–1518.4 ± 4.2	$CsUCl_6$		–1574.4 ± 2.5			
			Cs_2UCl_6		–2010.5 ± 4.2						
$Cs_2NaNpCl_6$		–2217.2 ± 3.1	Cs_2NpCl_6	*410 ± 15*	–1976.2 ± 1.9						
$Cs_2NaPuCl_6$	*440 ± 15*	–2294.2 ± 2.6	Cs_2PuCl_6	*412 ± 15*	–1982.0 ± 5.0						
Cs_3PuCl_6	*455 ± 11*	–2364.4 ± 9.0									
$CsPu_2Cl_7$	*424 ± 7*	–2399.4 ± 5.7									
$Cs_2NaAmCl_6$	*421* ± 15	–2315.8 ± 1.8									
$Cs_2NaCmCl_6$		*–2325 ± 7*									
$Cs_2NaBkCl_6$		*–2315* ± 7									
$Cs_2NaCfCl_6$		–2292.4 ± 5.8									
			Na_2UBr_6		–1529.7 ± 2.7						
K_2UBr_5		–1513.3 ± 4.5	K_2UBr_6		–1632.3 ± 2.7						
Rb_2UBr_5		–1528.8 ± 4.4	Rb_2UBr_6		–1653.7 ± 2.6						
Cs_2UBr_5		–1552.4 ± 4.9	Cs_2UBr_6		–1709.4 ± 2.6	$Cs_2UO_2Br_4$		–2008.7 ± 1.5			
			Cs_2NpBr_6	*469 ± 10*	–1682.3 ± 2.0						
			Cs_2PuBr_6	*470 ± 15*	–1697.4 ± 4.2						

[a] For the alpha form; $\Delta_f H^\circ(NaUF_6, \beta, 298.15\ K) = -(2708.3 \pm 5.4)\ kJ\ mol^{-1}$.
[b] For the alpha form; $\Delta_f H^\circ(NaUCl_6, \beta, 298.15\ K) = -(1472.1 \pm 29)\ kJ\ mol^{-1}$.
[c] Recalculated using $\Delta_f H^\circ(PaCl_4, cr, 298.15\ K)$ from Table 19.18.

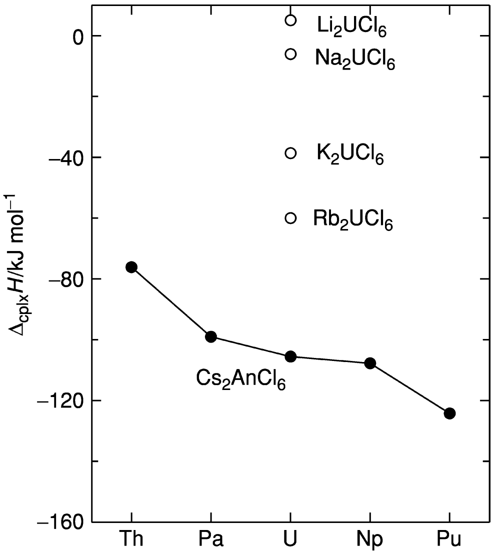

Fig. 19.27 *Enthalpies of complexation of complex actinide(IV) halides.*

enthalpy increments of UO_2X_2 (for X = F, Cl, and Br) have been measured by Cordfunke *et al.* (1979). Their data are in reasonable to good agreement with the low-temperature data. Cordfunke and Kubaschewski (1984) also cite unpublished experimental data for $UOCl_2$ and $U_2O_2Cl_5$ by Cordfunke, and estimated the heat capacity functions of other oxyhalides. They are listed in Table 19.28.

In contrast, data for mixed nitride halides are scarce. Recently Akabori *et al.* (2002) and Huntelaar *et al.* (2002) have presented data for the enthalpy of formation, the entropy, and high-temperature heat capacity of UNCl, which are included in Tables 19.27 and 19.28.

19.7.3 Gaseous oxyhalides

Several oxyhalides are stable in the gaseous phase and experimental vapor pressure data have been reported for UO_2F_2, UOF_4, and UO_2Cl_2 from which the enthalpies of formation of the gaseous molecules can be derived. In the NEA-TDB review, these studies were analyzed by third-law method using estimated molecular parameters from Glushko *et al.* (1978). The estimates for structure parameters and vibrational frequencies of UO_2F_2 differ considerably from those obtained by Privalov *et al.* (2002) using quantum chemical calculations at different theoretical levels (SCF, B3LYP). Souter and Andrews (1997) identified the molecules UO_2F_2, UOF_4, and UO_2F by infrared matrix-isolation spectroscopy. The asymmetric O–U–O stretching frequency found is in reasonable

Table 19.27 *Thermodynamic properties of crystalline actinide oxyhalides and complex actinide oxyhalides; estimated values are in italics.*

	S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)		S° (298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H^\circ$ (298.15 K) ($kJ\ mol^{-1}$)	*References*
			$ThOF_2$	*101.3 ± 8.4*	–1669.4 ± 10.5							a
			UOF_2	119.2 ± 4.2	–1504.6 ± 6.3				UO_2F_2	135.56 ± 0.42	–1653.5 ± 1.3	b
									UOF_4	*195 ± 5*	–1924.6 ± 4.0	b
PuOF	*96 ± 10*	*–1140 ± 20*										b
			$ThOCl_2$	114.6 ± 4.2	–1232.6 ± 8.4							a
			$PaOCl_2$	*125.5 ± 8.4*	*–1096 ± 9*							a
UOCl	*102.5 ± 8.4*	–833.9 ± 4.2	$UOCl_2$	138.32 ± 0.21	–1069.3 ± 2.7	$UOCl_3$	*170.7 ± 8.4*	–1140.0 ± 8.0	UO_2Cl_2	150.54 ± 0.31	–1243.6 ± 1.3	b
			$U_2O_2Cl_5$	*326.3 ± 8.4*	–2197.4 ± 4.2	UO_2Cl	*112.5 ± 8.4*	–1171.1 ± 8.0				b
						$U_5O_{12}Cl$	*465 ± 30*	–5854.4 ± 8.6				b
			$NpOCl_2$	*143.5 ± 5.0*	–1030.0 ± 8.0							b
PuOCl	105.6 ± 3.0	–931.0 ± 1.7										b
AmOCl	*92.6 ± 10*	–949.8 ± 6.0										b
CmOCl	*105 ± 21*	–963.2 ± 6.7										a
BkOCl		*–944 ± 10*										c
CfOCl		–920 ± 7										c
			$ThOBr_2$	*129.7 ± 12.6*	–1129.7 ± 12.6							a
			$PaOBr_2$	*142.3 ± 16.7*	–1002.9 ± 15.5							a,d
			$UOBr_2$	157.57 ± 0.29	–973.6 ± 8.4	$UOBr_3$	*205.0 ± 12.6*	–954 ± 21	UO_2Br_2	169.5 ± 4.2	–1137.4 ± 1.3	b
PuOBr	*127 ± 10*	–870.0 ± 8.0										b
AmOBr	*104.9 ± 12.8*	–887.0 ± 9.0										
			$ThOI_2$	*144.8 ± 4.2*	–996.6 ± 2.5							a
PuOI	*130 ± 15*	*–802 ± 20*										b
			UNCl	96.54 ± 0.10	–559 ± 4							e

[a] Fuger *et al.* (1983).
[b] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[c] Burns *et al.* (1998).
[d] Recalculated with the accepted value for $\Delta_f H^\circ(Pa^{4+}$, aq, 298.15 K).
[e] Huntelaar *et al.* (2002) and Akabori *et al.* (2002).

Table 19.28 *High-temperature heat capacity of the crystalline uranium oxyhalides and oxynitrides;* $C_p/(J\ K^{-1}\ mol^{-1}) = a(T/K)^{-2} + b + c(T/K)$ (*estimated values are in italics*).

	$a\ (\times 10^{-6})$	b	$c\ (\times 10^{3})$	T_{max} (K)	*References*
UO_2F_2	–1.0208	106.238	28.326		a
UO_2Cl_2	–1.1418	115.275	18.2232		a,b
UO_2Br_2		104.270	37.938		a,b
UNCl	–0.97344	79.7373	2.3703	1000	c

[a] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[b] Cordfunke and Ouweltjes (1981).
[c] Huntelaar *et al.* (2002).

Table 19.29 *Thermodynamic properties of some gaseous oxyhalides; estimated vales are given in italics.*

	$S°$(298.15 K) ($J\ K^{-1}\ mol^{-1}$)	$\Delta_f H°$(298.15 K) ($kJ\ mol^{-1}$)	*References*
UO_2F_2	342.7 ± 6.0	–1352.5 ± 10.1	a
UOF_4	363.2 ± 8.0	–1763 ± 20	a
UO_2Cl_2	373.4 ± 6.0	–970.3 ± 15.0	a

[a] NEA-TDB (Grenthe *et al.*, 1992; Silva *et al.*, 1995; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

agreement with the B3LYP results of Privalov *et al.* (2002), which also give the best agreement with the estimates used in the NEA-TDB review. The recommended values of the NEA-TDB review for the species UO_2F_2, UOF_4, and UO_2Cl_2 are given in Table 19.29.

19.8 HYDRIDES

19.8.1 Enthalpy of formation

The enthalpies of formation of the actinide hydrides have been principally derived from hydrogen pressure measurements in which the pressure–temperature–composition relation was studied. The equilibrium reaction in these metal–hydrogen systems can be described as:

$$\left(\frac{2}{2-s-x}\right)\mathrm{AnH}_s + \mathrm{H}_2 = \left(\frac{2}{2-s-x}\right)\mathrm{AnH}_{2-x} \qquad (19.28)$$

where s and $(2-x)$ both generally have the values 1.3, 2, 3, and 3.75. The AnH_2 compounds occur in all systems from Th to Cm, except U. In the U–H system, only the trihydride occurs, which is also found in the systems with Np, Pu, and

Am, though almost no data exist for the latter. The composition H/An = 1.3 is typical for the Pa–H system, and H/An = 3.75 for the Th–H system.

Flotow *et al.* (1984) systematically analyzed the equilibrium data for Th, Pa, U, Np, Pu, and Am, and their recommended enthalpies of formation for the hydrides of Th, Pa, U, and Pu are summarized in Table 19.30. Ward *et al.* (1987) measured the hydrogen dissociation pressure in the Np–H and derived thermodynamic data for NpH_2, $NpH_{2.6}$, and NpH_3. Gibson and Haire (1990) measured the hydrogen dissociation pressures of milligram-sized samples of the americium and curium hydrides, and made comparison to the lanthanide hydrides (Dy, Ho). Their results for AmH_2 are in good agreement with the recommended values by Flotow *et al.* (1984), who selected the average results of two discordant studies; their results for CmH_2 are the first ones to be reported. They have been included in Table 19.30. The variation of the enthalpy of formation of the actinide dihydrides is shown in Fig. 19.28, together with the data for the lanthanide dihydrides (Libowitz and Maeland, 1979). As observed for the elements and many compounds, the trend in light actinides dihydrides is significantly different from that of the lanthanides and the two curves approach each other near Am and Cm.

19.8.2 Entropy

Low-temperature heat capacity measurements (up to 300 K) have been reported for ThH_2, $ThH_{3.75}$, UH_3, and $PuH_{1.9}$ and the entropy values at 298.15 K recommended by Flotow *et al.* (1984) are listed in Table 19.30. The entropies of the other compounds have been derived by Flotow *et al.* (1984) from the high-temperature hydrogen equilibrium measurements, using estimated heat capacity data. Flotow *et al.* (1984) also estimated the entropy of CmH_2 by linear extrapolation of the data of the dihydrides of Np, Pu, and Am, but it is doubtful whether this is correct in view of the trend shown for the enthalpies of formation, which indicates that CmH_2 resembles more the lanthanide dihydrides than the light actinide dihydrides.

19.8.3 High-temperature properties

High-temperature heat capacity data have been reported only for PuH_2 (Oetting *et al.*, 1984). The high-temperature heat capacity of ThH_2, $ThH_{3.75}$, and UH_3 were calculated by Flotow *et al.* (1984). They described the total heat capacity as the sum of the electronic, optical mode, and residual contributions:

$$C_p = C_{ele} + C_{\mu H} + C_{residual} \tag{19.29}$$

where the electronic heat capacity coefficient and the residual term were obtained from the low-temperature measurements, which extent to 350 K, and

Table 19.30 *Enthalpies of formation and entropies of the crystalline actinide hydrides, estimated values are given in italics.*

	AnH_2		AnH_3		$AnH_{3.75}$		
	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$ (298.15 K) (kJ mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	$S°$ (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
Th	50.73 ± 0.10	–145.1 ± 1.0			54.43 ± 0.13	–215.8 ± 4.3	a
Pa							
U			63.68 ± 0.13	–127.0 ± 0.13			a
Np	*66.1*	–119		–230.9 ± 3.3			b
Pu	72.84 ± 0.38	–164.4		*–236.4*			a
Am	*48.1*	–177 ± 12					a,c
Cm		–187 ± 14					c

[a] Flotow *et al.* (1984).
[b] Ward *et al.* (1987).
[c] Gibson and Haire (1990).

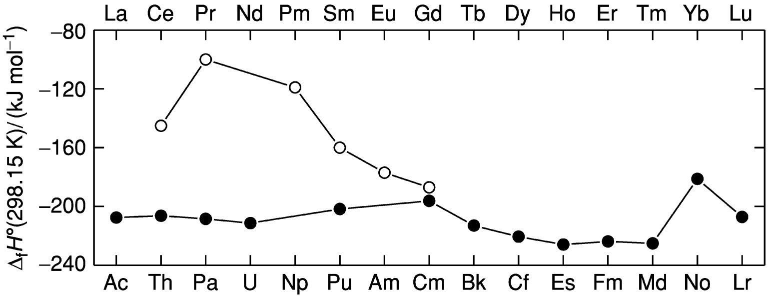

Fig. 19.28 *Enthalpies of formation of lanthanide* (•) *and actinide* (○) *dihydrides.*

Table 19.31 *High-temperature heat capacity of selected crystalline actinide hydrides;* $C_p/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a(T/\mathrm{K})^{-2} + b + c(T/\mathrm{K}) + d(T/\mathrm{K})^2$ (*estimated values are given in italics*), *from Flotow* et al. (1984).

	a (×10^{-6})	b	c (×10^3)	d (×10^6)	T_{max} (K)
ThH_2	–0.17364	166.566	149.725	–69.113	800
$ThH_{3.75}$		–192.918	272.726	–120.387	800
UH_3	–0.48392	6.05878	189.349	–87.514	800
NpH_2		32.4395	50.1072	–1.1138	900
PuH_2	2.1711	–78.1827	405.219	–264.995	600

the optical modes were obtained from spectroscopic measurements. Polynomial fits of the heat capacity function thus obtained by Flotow *et al.* for temperatures up to maximum 800 K are listed in Table 19.31.

19.9 HYDROXIDES AND OXYHYDRATES

19.9.1 Trihydroxides

(a) Enthalpy of formation

The only experimental determinations of the enthalpy of formation of a trivalent actinide hydroxide are two solution-calorimetry studies for $Am(OH)_3$, but the two results differ considerably (Morss and Williams, 1994; Merli *et al.*, 1997) due to a difference of enthalpies of solution of the trihydroxide of (23 ± 8) kJ mol^{-1}. The value selected in Table 19.32 is that calculated by Guillaumont *et al.* (2003), based primarily on the measured solubility product of $Am(OH)_3$ measured by Silva (1982) corrected for hydrolysis and ionic strength, and an estimated entropy of $Am(OH)_3$ (Guillaumont *et al.*, 2003). The selected value

Table 19.32 *Enthalpies of formation and entropies of the crystalline lanthanide and actinide trihydroxides; estimated values are given in italics.*

An(OH)$_3$	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*Ln(OH)*$_3$	$S°$(298.15 K) (J K^{-1} mol^{-1})[a]	$\Delta_f H°$(298.15 K) (kJ mol^{-1})
			$La(OH)_3$	117.81	–1415.6 ± 2.0[b]
			$Ce(OH)_3$	*130.2*	
			$Pr(OH)_3$	*132.6*	–1409.7 ± 4.9[c]
			$Nd(OH)_3$	129.87	–1415.6 ± 2.3[b]
			$Pm(OH)_3$	*131.2*	*–1419 ± 10*[d]
$Pu(OH)_3$	*134 ± 8*[e]		$Sm(OH)_3$	*126.7*	–1406.6 ± 2.2[b]
$Am(OH)_3$	*116 ± 8*[f]	–1353.2 ± 6.4[f]	$Eu(OH)_3$	119.88	*–1319 ± 10*[d]
$Cm(OH)_3$	*134 ± 8*[e]		$Gd(OH)_3$	126.63	*–1409 ± 10*[d]
$Bk(OH)_3$			$Tb(OH)_3$	128.37	*–1415 ± 10*[d]
$Cf(OH)_3$			$Dy(OH)_3$	*130.0*	*–1428 ± 10*[d]
$Es(OH)_3$			$Ho(OH)_3$	130.04	*–1431 ± 10*[d]

[a] As compiled by Konings (2001a).
[b] Merli *et al.* (1997).
[c] Morss and Hall (1994); Diakonov *et al.* (1998b) recommend –(1414 ± 10) kJ mol^{-1}.
[d] Diakonov *et al.* (1998a,b).
[e] Following the procedure of Guillaumont *et al.* (2003), p. 350, for $S°(Am(OH)_3,cr) = S_{lat} + S_{exc}$ using data from Konings (2001a) and estimating S_{exc} from that of sesquioxides Pu_2O_3 and Cm_2O_3.
[f] Guillaumont *et al.*(2003).

is nearly consistent with the experimental value of Merli *et al.* (1997), $\Delta_f H°(M(OH)_3,cr) = -(1343.6 \pm 1.8)$ kJ mol^{-1}. Their sample was well characterized and their calorimetric results are supported by similar measurements that they carried out for lanthanide hydroxides, which are consistent with solubility data.

(b) Entropy

The entropies of the solid trihydroxides $An(OH)_3$ have been estimated using the approach outlined earlier (equation (19.10)) (Konings, 2001a). The lattice component was estimated from the lanthanide trihydroxides, assuming the displacement of the trend to be the same as for the sesquioxides. The excess entropy was calculated from the degeneracy of the ground state. The values thus obtained are listed in Table 19.32 together with data for the lanthanide trihydroxides.

(c) Solubility products

Solubility products, often denoted ‘solubility constants,’ refer to equilibria such as:

$$M(OH)_3(cr) = M^{3+}(aq) + 3\,OH^-(aq), \quad K = K^0_{s,0} \tag{19.30}$$

Because americium has important long-lived isotopes and because it exists in solution as Am(III), its hydrolysis and solubility in aqueous solutions have been the most carefully studied of the An(III) ions. The NEA review (Guillaumont *et al.*, 2003) selected the value of (15.6 ± 0.6) for the equilibrium

$$\mathrm{Am(OH)_3(cr)} + 3\ \mathrm{H^+(aq)} = \mathrm{Am^{3+}(aq)} + 3\,\mathrm{H_2O(l)}, \quad K = {}^*K^0_{\mathrm{s,0}} \qquad (19.31)$$

from the study of Silva (1982) because the solid phase in equilibrium with the solution was crystalline $Am(OH)_3$. The asterisk (*) in this notation refers to the protonation that is part of the equilibrium. For this equilibrium at 298.15 K, $\log_{10} K^0_{\mathrm{s,0}} = \log_{10} {}^*K^0_{\mathrm{s,0}} - 3\log_{10} K_{\mathrm{w}} = 15.6 - 3 \times 14 = -26.4$. Guillaumont *et al.* (2003) also selected the value $\log_{10} {}^*K^0_{\mathrm{s,0}} = (16.9 \pm 0.8)$ for the equilibrium (equation (19.31)) with $Am(OH)_3$(am), where 'am' refers to the precipitate that was amorphous to X-rays after aging for 4 months.

Latimer (1952) estimated the solubility products of actinide(III) hydroxides, $An(OH)_3$, from corresponding values for freshly precipitated hydroxides of the lanthanides. It is well known that, as these gelatinous precipitates age, their crystallinity increases and their solubility product decreases, so that the aged precipitates more nearly reflect equilibrium conditions. Baes and Mesmer (1976) exhaustively surveyed the literature and evaluated heterogeneous equilibria for lanthanide and actinide hydroxides and hydrated oxides. Additional thermochemical and extensive solubility data are available for the lanthanide trihydroxides. Diakonov *et al.* (1998a,b) carried out an extensive critical review of the thermochemical and solubility literature on rare earth hydroxides. These authors showed that there is a systematic trend of $\log_{10} K^0_{\mathrm{s,0}}$ data for all rare earth hydroxides as a function of M^{3+} ionic radii. Specifically, the values of solubility product $\log_{10} K^0_{\mathrm{s,0}}$ and $\log_{10} {}^*K_{\mathrm{s,0}}$ become more positive as Z increases, because the ionic radii decrease and the Ln^{3+} ions become more acidic.

This trend could be extended to estimate solubility products for actinide trihydroxides. After the review of Diakonov *et al.* was published, Cordfunke and Konings (2001c) critically reviewed all the literature on enthalpy of formation of rare earth aqueous ions and recommended a set of values that are more comprehensive than the enthalpies of formation of rare earth aqueous ions used by Diakonov *et al.* One could use the recommended values of Diakonov *et al.*, with corrections for Cordfunke and Konings enthalpies of formation of rare earth aqueous ions, to extrapolate the relation between $\{\Delta_f H^\circ(\mathrm{M(OH)_3,cr}) - \Delta_f H^\circ(\mathrm{M^{3+}, aq})\}$ and the M^{3+} ionic radii to derive estimates of $\log_{10} {}^*K_{\mathrm{s,0}}$ for $An(OH)_3$. However, the one 'anchor,' $Am(OH)_3$, has such a significant uncertainty that such an extrapolation is considered too speculative for this chapter. Because the calorimetric data of Merli *et al.* for $Am(OH)_3$ are not quite in agreement with solubility data, enthalpy and entropy estimates for other actinide trihydroxides were not used to estimate solubility product measurements for other actinide trihydroxides in this chapter. We do cite the value of $\log_{10} {}^*K_{\mathrm{s,0}} = (15.8 \pm 1.5)$ calculated for $Pu(OH)_3$ (Felmy *et al.*, 1989). This value is slightly smaller than the estimate for $Am(OH)_3$ cited above, consistent with the systematic trend for rare earth hydroxides as a function of ionic radius.

19.9.2 Oxides, hydrated oxides, and oxyhydroxides of An(IV), An(V), and An(VI)

The thermodynamics of crystalline anhydrous oxides was discussed in Section 19.5. Therefore, for these compounds, only solubility product values of interest are mentioned here for comparison with those of the amorphous corresponding compounds.

Under basic conditions, all actinide ions precipitate as hydroxides or hydrated oxides. Very few of these precipitates have been thoroughly characterized; interpolations, extrapolations, and approximations are usually necessary. Lemire *et al.* (2001) and Guillaumont *et al.* (2003) evaluated the literature results on the solubilities of some amorphous and crystalline actinide oxides, hydrated oxides, and oxyhydroxides. Their recommended values are given in Table 19.33. In this table the solubility product refers to the equilibrium constant for reactions such as

$$MO_2(\text{am or cr}) + 2\ H_2O\,(l) = M^{4+}(aq) + 4\ OH^-(aq), \quad K = K^0_{s,0} \quad (19.30a)$$

$$NpO_2OH(am) + H^+(aq) = NpO_2^+(aq) + H_2O(1), \quad K = {}^*K^0_{s,0} \quad (19.31a)$$

As mentioned in equation (19.31), the asterisk (*) in this notation refers to the protonation that is part of the equilibrium.

Selections were also made (Grenthe *et al.*, 1992; Guillaumont *et al.*, 2003) for other hydrates of UO_3. We cite here two properties of $UO_3 \cdot 2H_2O(cr)$ ('schoepite'): $S°(298.15) = (188.54 \pm 0.38)$ J K^{-1} mol^{-1} and $\Delta_f H°(298.15) = -(1826.1 \pm 1.7)$ kJ mol^{-1}, as given by NEA-TDB (Grenthe *et al.*, 1992) based on measurements by Tasker *et al.* (1988). The solubility product of this compound is given in Table 19.33. We note that $UO_3 \cdot 2H_2O(cr)$, which is often called schoepite, should be referred to as metaschoepite (Finch *et al.*, 1998).

The enthalpy of formation of the uranium(VI) peroxide studtite, $(UO_2)O_2(H_2O)(cr)$, has been determined to be $-(2344.7 \pm 4.0)$ kJ mol^{-1} (Hughes-Kubatko *et al.*, 2003). The authors calculated the solubility at 298.15 K,

$$UO_2^{2+}\,(aq) + H_2O_2(aq) + 4\,H_2O(l) = (UO_2)O_2(H_2O)(cr) + 2\,H^+(aq) \quad (19.33)$$

and concluded that this peroxide is stable under the conditions where aqueous peroxide is formed from radiolysis of water by alpha particles.

The enthalpy of formation of $NpO_2OH(am)$ was selected as $-(1222.9 \pm 5.5)$ kJ mol^{-1} by Lemire *et al.* (2001) from enthalpy of solution measurements by two different groups (Campbell and Lemire, 1994; Merli and Fuger, 1994) who used material containing different amounts of water.

The enthalpy of formation of $UO_3 \cdot H_2O(\beta)$ was selected as $-(1533.8 \pm 1.3)$ kJ mol^{-1} by Grenthe *et al.* (1992) from the difference in the enthalpy of solution of this compound (Cordfunke, 1964) and that of γ-UO_3. The enthalpy of formation of $NpO_3 \cdot H_2O(cr)$ ($= NpO_2(OH)_2(cr)$) was selected as $-(1377 \pm 5)$ kJ mol^{-1}

Table 19.33 *Solubility products of the actinide crystalline and amorphous oxides at* 298.15 K, *from NEA-TDB* (*Grenthe* et al., 1992; *Silva* et al., 1995; *Lemire* et al., 2001; *Guillaumont* et al., 2003).

Solid phase	*Equilibrium*	*Th*	*U*	*Np*	*Pu*	*Am*
$An(OH)_3$(am)	$\log_{10}K^0_{s,0}$					–(25.1 ± 0.8)
$An(OH)_3$(cr)	$\log_{10}K^0_{s,0}$				–(26.2 ± 1.5)	–(26.4 ± 0.6)
AnO_2(am)	$\log_{10}K^0_{s,0}$	–(47.0 ± 0.8)	–(54.5 ± 1.0)	–(56.7 ± 0.5)	–(58.33 ± 0.52)	
AnO_2(cr)	$\log_{10}K^0_{s,0}$	–(54.3 ± 1.1)	–(60.86 ± 0.36)	–(65.75 ± 1.07)	–(64.04 ± 0.51)	–(65.4 ± 1.7)
An_2O_5(cr)	$\log_{10}{}^*K_{s,0}$			+(1.8 ± 0.8)		
AnO_2OH(am) 'fresh'	$\log_{10}{}^*K_{s,0}$			+(5.3 ± 0.2)		+(5.3 ± 0.5)
AnO_2OH(am) 'aged'	$\log_{10}{}^*K_{s,0}$			+(4.7 ± 0.5)	+(5.0 ± 0.5)	
$AnO_3 \cdot H_2O(\beta)$	$\log_{10}{}^*K_{s,0}$		+(4.90 ± 0.50)	+(5.47 ± 0.40)	+(5.80 ± 1.00)	
$AnO_3 \cdot 2H_2O$(cr)	$\log_{10}{}^*K_{s,0}$		+(4.81 ± 0.43)		+(5.5 ± 1.0)	

by Lemire *et al.* (2001), primarily from the enthalpy of solution measurements by Fuger *et al.* (1969).

No other hydroxides of tetravalent or higher-valent actinides have been adequately characterized for thermodynamic property determinations and calculations of solubility at equilibrium conditions.

19.9.3 Gaseous oxyhydroxides

It has been shown by several authors that the volatility of the uranium oxides is significantly enhanced in the presence of water vapor, as a result of the formation of the gaseous species $UO_2(OH)_2$ (Dharwadkar *et al.*, 1975; Krikorian *et al.*, 1993a). The equilibrium data of these studies were analyzed in the NEA-TDB review (Guillaumont *et al.*, 2003) using second- and third-law methods to derive the enthalpy of formation. The agreement between the studies is very poor. Moreover, the thermal functions for the third-law analysis, obtained from two sets of estimated molecular parameters (Ebbinghaus, 1995; Gorokhov and Sidorova, 1998), result in appreciably different entropy values. For that reason no selected values were presented by NEA-TDB. Recently, Privalov *et al.* (2002) calculated the geometry and vibrational frequencies of $UO_2(OH)_2$ using quantum chemical techniques. The thermodynamic functions calculated from their results are close to those of Gorokhov and Sidorova (1998). Also an increased volatility was reported in the presence of steam for the oxides of Pu and Am (Krikorian *et al.*, 1993b).

19.10 CARBIDES

The thermodynamic properties of the binary actinide carbides in the Th–C, U–C, Np–C, Pu–C, and Am–C systems were reviewed by Holley *et al.* (1984) as part of the IAEA series on the chemical thermodynamics of the actinide elements and compounds. In the NEA-TDB series that covers the compounds from U to Am (Grenthe *et al.*, 1992; Lemire *et al.*, 2001), most of the data by Holley *et al.* (1984) were accepted unchanged. Solid dicarbides, sesquicarbides, and monocarbides of the actinides have all been reported to exist, all generally showing wide ranges of nonstoichiometry, which makes the comparison of the different experimental results difficult. For the Pu–C system also, the compound Pu_3C_2 has been found.

19.10.1 Solid carbides

(a) Enthalpy of formation

The dicarbide exists in the Th–C and U–C systems with certainty, and in the Pu–C system only at high temperatures. The situation for the Pa–C and Np–C systems is not yet fully clear, but claims for the synthesis of the dicarbides have been made. The measurements for thorium and uranium dicarbide have all been made on samples that are slightly substoichiometric ($C/M \approx 1.90$–1.97), and contain variable amount of oxygen impurities. Holley *et al.* (1984) gave recommended values for the composition $C/M = 1.94$ for both Th and U, probably the most stable composition, based on an analysis of the high-temperature equilibria and combustion calorimetry, which are given in Table 19.34.

The sesquicarbide is known for the U–C, Np–C, Pu–C, and Am–C systems, and measurements of the enthalpies of formation are only known for the first three compounds. Of these compounds, U_2C_3 is probably not thermodynamically stable at room temperature (its lower stability limit is estimated to be 1200 K) but samples have been cooled down without difficulty. High-temperature equilibria and combustion calorimetry have been reported, data which were analyzed by Holley *et al.* (1984). The value for Np_2C_3 is based on a preliminary measurement by combustion calorimetry; for U_2C_3 and Pu_2C_3 the combustion values at 298.15 K were slightly adjusted by Holley *et al.* (1984) to get a reasonable agreement with the high-temperature Gibbs energy values. From these values, Holley *et al.* (1984) estimated the enthalpy of formation of Am_2C_3 as $\Delta_f H°(298.15\ \mathrm{K}) = -(151 \pm 42)\ \mathrm{kJ\ mol^{-1}}$.

The monocarbides are best described by the formula MC_{1-x}; they are known for all actinide–carbon systems from Th to Pu. The boundary compositions are $ThC_{0.98}$, UC, $NpC_{0.94}$, and $PuC_{0.84}$ and the enthalpies of formation of compositions, close to those recommended by Holley *et al.* (1984), are included in Table 19.34.

The enthalpy of formation of Pu_3C_2 was calculated by Holley *et al.* (1984) from phase considerations: (i) Pu_3C_2 is stable with respect to Pu and $PuC_{0.88}$ from 300 to 800 K and (ii) Pu_3C_2 decomposes to Pu and $PuC_{0.78}$ at 848 K.

(b) Entropy

A relatively large number of low-temperature heat capacity measurements have been made for the actinide carbides. For the Pu–C system measurements for 16 compositions have been reported, with reasonable though not complete consistency (see Holley *et al.*, 1984). Thus most of the entropy values listed in Table 19.34 are based on experimental studies; exceptions are Np_2C_3 and Pu_3C_2. Most of the experimental values have been corrected for the randomization entropy:

$$S_{\mathrm{ran}} = x\ \ln\ x - (1-x)\ln(1-x) \qquad (19.32)$$

which arises from the random ordering of the carbon and vacancies in the monocarbide, and of C and C_2 groups in the dicarbides.

Table 19.34 *Enthalpies of formation and entropies of the crystalline actinide carbides, pnictides and chalcogenides; see text for reference* (*estimated values are given in italics*). *The values for the compounds thorium are from the IAEA reviews* (*Chiotti* et al., 1981; *Holley* et al., 1984), *those for the compounds uranium, neptunium, and plutonium are from NEA-TDB* (*Grenthe* et al., 1990*; Lemire* et al., 2001*; Guillaumont* et al., 2003), *the values for* Am_2C_3 *are from Holley* et al. (1984).

	Th		*U*		*Np*		*Pu*		*Am*	
	$S°$ (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$ (298.15 K) (kJ mol^{-1})	$S°$ (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$ (298.15 K) (kJ mol^{-1})	$S°$ (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$ (298.15 K) (kJ mol^{-1})	$S°$ (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$ (298.15 K) (kJ mol^{-1})	$S°$ (298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$ (298.15 K) (kJ mol^{-1})
An_3C_2							*210 ± 5*	*–113.0*		
AnC_{1-x}	59.0 ± 2.0	–125.5 ± 6.3	59.3 ± 0.2	–97.9 ± 4.0	72.2 ± 2.4	–71.1 ± 10.0	74.8 ± 2.1	–45.2 ± 8.0		
An_2C_3			137.8 ± 0.3	–183.3 ± 10.0	*135 ± 10*	–187.4 ± 19.2	*150 ± 2.9*	–149.4 ± 16.7	145 ± 20	–151 ± 42
$AnC_{1.94}$	70.4 ± 6.7	–125.5 ± 6.7	68.3 ± 2.0	–87.2 ± 2.1						
AnN	56.1 ± 0.8	–378 ± 10	62.43 ± 0.22	–290.0 ± 3.0	*63.9 ± 3.0*	*–305 ± 10*	64.81 ± 1.50	–299.2 ± 2.5		
$AnN_{1.466}$			*64.5 ± 1.0*	–362.2 ± 2.3						
An_3N_4	182.8 ± 2.1	–1305 ± 25								
AnP			78.28 ± 0.42	–269.8 ± 11.1			81.32 ± 6.00	–318 ± 21		
An_3P_4			259.4 ± 2.6	–843 ± 26						
AnP_2			100.7 ± 3.2	–304 ± 15						
AnAs			97.4 ± 2.0	–234.3 ± 8.0			94.3 ± 7.0	–240 ± 20		
An_3As_4			309.07 ± 0.60	–720 ± 18						
$AnAs_2$			123.05 ± 0.20	–252 ± 13						
AnSb					101.4 ± 6.1		106.9 ± 7.5	–150 ± 20		
$AnSb_2$			141.46 ± 0.13	–173.6 ± 10.9						
An_3Sb_4			349.8 ± 0.4	–451.9 ± 22.6						

(c) High-temperature properties

Enthalpy increment measurements have been reported for the three uranium carbides as well as PuC and Pu_2C_3. All data show a steep rise in the derived heat capacity above 1200 K, as is also observed in the oxides and nitrides and which have been attributed to the contribution of lattice vacancies. Fig. 19.29 shows the heat capacity of the three uranium carbides indicating rather similar behavior. Holley *et al.* (1984) estimated the heat capacity of ThC and ThC_2 from these data assuming a similar shape of the C_p curve. The heat capacity equations are summarized in Table 19.35.

19.10.2 Gaseous carbides

Gupta and Gingerich (1979, 1980) have detected gaseous AnC_n molecules with $n = 1$ to 6 in the Th–C and U–C systems by mass spectrometry. In the Th–C system, the molecules ThC_2 and ThC_4 contribute significantly to the vapor pressure, and in the ThC_2–C region the contribution of the former is about equal to that of Th(g). In the U–C system, only UC_2 has significant contribution for thermodynamic measurements. Holley *et al.* (1984) give estimated molecular properties for the thorium compounds ThC_2 and ThC_4 from which the thermal functions have been calculated. They assume a linear Th–C–C structure for ThC_2 and a linear C_2–Th–C_2 structure for ThC_4. With these functions they derived the enthalpies of formation of these molecules using third-law analysis. The resulting values are given in Table 19.36. Such treatment was not followed for UC_2 because of insufficient and inconsistent information.

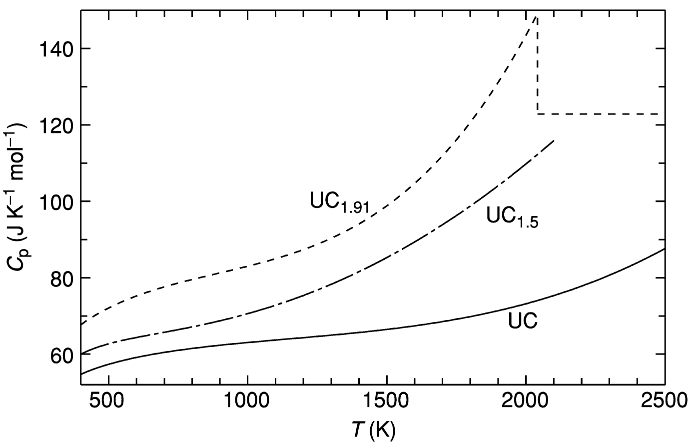

Fig. 19.29 *The high-temperature heat capacity of the uranium carbides.*

Table 19.35 *High-temperature heat capacity of the crystalline actinide nitrides and carbides;* $C_p/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a(T/\mathrm{K})^{-2} + b + c(T/\mathrm{K}) + d(T/\mathrm{K})^2 + e(T/\mathrm{K})^3$ *(estimated values in italics); temperature* T_{max} *indicates the transition or melting temperature except values in brackets, which indicate the maximum valid temperature of the polynomial equation.*

	a ($\times10^{-6}$)	b	c ($\times10^{3}$)	d ($\times10^{6}$)	e ($\times10^{9}$)	T_{max} (K)	$\Delta_{trs}H$ (kJ mol^{-1})	*References*
ThC	*–0.6276*	*46.024*	*25.522*	*–18.828*	*5.439*	[2270]		a
$ThC_{1.94}$	*–0.5858*	*44.769*	*83.68*	*–79.496*	*30.426*	[1700]		a
UC	–0.618395	50.9235	25.7065	–18.6711	5.71334	2780		a
U_2C_3	–2.90503	150.6366	–47.8717	41.3588		[2100]		a
$UC_{1.91}$	–0.59258	48.9654	82.4867	–78.1086	30.2671	2041	10.083	a
		122.88						a
$PuC_{0.84}$	–0.15659	57.848	–14.4904	7.7048	8.6115	[1875]		a
Pu_2C_3	–0.5200	156.0004	–79.8726	70.4167		2285		a
ThN	*–0.4787*	*47.447*	*9.523*			[2000]		b
Th_3N_4	*–2.230*	*164.557*	*26.108*			[2000]		b
UN	–0.23304	40.4263	41.1928	–31.3066	10.0570	3123		c
$UN_{1.54}$	*–1.6788*	*65.040*	*19.288*			[1700]		d
PuN		45.002	15.420			[2000]		e
NpN	–0.0908	43.3	23.1	–7.62		[2000]		f

[a] Holley *et al*. (1984).
[b] Rand (1975).
[c] Refit of the equation by Hayes *et al*. (1990).
[d] Tagawa (1974).
[e] Lemire *et al*. (2001).
[f] Nakajima and Arai (2003).

Table 19.36 *Thermodynamic properties of the gaseous actinide carbides; estimated values are given in italics, from Holley* et al. (1984).

	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})
ThC_2	256.7	720.5 ± 33.5
ThC_4	294.0	855.6 ± 41.8

19.11 PNICTIDES

The planned volume on the actinide pnictides in the IAEA series on the chemical thermodynamics of the actinide elements and compounds has not been completed and as a result a systematic review of the actinide nitride series is not available. However, in the NEA-TDB series, the data for the nitride compounds of uranium, neptunium, and plutonium have been reviewed, but with emphasis on the room temperature data.

19.11.1 Solid nitrides

(a) Enthalpy of formation

The enthalpies of formation of the mononitrides for ThN, UN, and PuN are based on calorimetric studies, as are those of the sesquinitrides $UN_{1.5+x}$ (α-U_2N_3) and $UN_{1.466}$ (β-U_2N_3) and Th_3N_4. The selected data for the compounds of U and Pu, which are summarized in Table 19.34, are from the NEA-TDB reports (Grenthe *et al.*, 1992; Lemire, *et al.*, 2001; Guillaumont *et al.*, 2003), the value of ThN and Th_3N_4 are taken from the assessment by Rand (1975).

The measurements for the uranium nitrides have not been made for the stoichiometric compositions as these are often difficult to prepare or do not exist: in α-U_2N_3, the N/U ratio varies from 1.54 to 1.75, in β-U_2N_3 from 1.45 to 1.49. The enthalpies of formation of the various uranium nitrides vary linearly as a function of the N/U ratio, as shown in Fig. 19.30. Thus the enthalpy of formation of α-U_2N_3 is represented by the following equation:

$$\Delta_f H°(UN_{1.5+x},\ \text{cr},\ 298.15\ \text{K})/\text{kJ mol}^{-1} = -366.7 - 138.2x$$

which is a simple linear representation of the two compositions with N/U 1.606 and 1.674 for which experimental measurements have been made (see Grenthe *et al.*, 1992).

The enthalpy of formation of ThN is significantly more negative than that of UN and PuN. This can be explained by the fact that the chemical bonding in ThN is less ionic and more covalent than in UN and PuN. Kuznietz (1968)

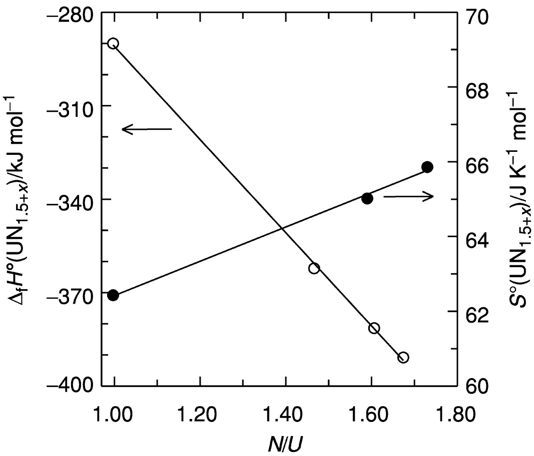

Fig. 19.30 *The enthalpy of formation* (○) *and the standard entropy* (•) *of the uranium nitrides as a function of the N/U ratio.*

proposed that the ThN lattice consists of Th^{4+} and N^{3-} ions with one conduction electron for each Th atom. Recently some indirect information on the enthalpies of formation of the mononitrides NpN and AmN was obtained from high-temperature Knudsen cell studies. Nakajima *et al.* (1997, 1999a) studied the vaporization of NpN and (Np,Pu)N. From their results, they found that the Gibbs energy of formation of NpN is between the values for UN and PuN. This is a justification for the approach of Lemire *et al.* (2002) who estimated the enthalpy of NpN by interpolation of the values for UN and PuN. Ogawa *et al.* (1995) studied the vaporization of PuN containing small amount of ^{241}Am as decay product. From these results, they estimated the enthalpy of formation of AmN as −294 kJ mol^{-1} at 1600 K.

(b) Entropy

Low-temperature heat capacity measurements of three mononitrides have been reported: ThN, UN, and PuN. As is the case for the enthalpies of formation, the value for ThN is distinctly different (lower) from that of UN and PuN. Lemire *et al.* (2001) assumed the entropy of NpN to be between the values for UN and PuN. Low-temperature heat capacity measurements have also been reported for Th_3N_4 and α-U_2N_3 (two compositions with N/U 1.59 and 1.73). The recommended values are summarized in Table 19.34. Like the enthalpy of formation, the standard entropy varies linearly with the N/U ratio, as shown in Fig. 19.30, and the value for $UN_{1.466}$ is obtained by interpolation. Based on this observation, the standard entropy of α-U_2N_3 is represented by the following equation:

$$S^\circ(\mathrm{UN}_{1.5+x},\ \mathrm{cr},\ 298.15\ \mathrm{K})/\mathrm{J\ K^{-1}\ mol^{-1}} = 64.48 + 6.00x$$

(c) High-temperature properties

The high-temperature properties of UN and PuN were reviewed by Matsui and Ohse (1987), those of UN by Hayes *et al.* (1990), and more recently by Chevalier *et al.* (2000). These are the only two mononitrides for which calorimetric enthalpy increment measurements are available. Below 1700 K, the UN data recommended by Matsui and Ohse (1987) and Hayes *et al.* (1990) are in good agreement, as they are based on the same set of experimental data. But Hayes *et al.* (1990) indicate that UN shows a nonlinear increase in the heat capacity at high temperatures, likely due to the contribution of lattice defects, based on measurements by Conway and Flagella (1969), which were not considered by Matsui and Ohse (1987). This effect has not been observed in PuN, but the experimental data for this compound are limited to 1560 K. This situation is similar to the dioxides. Kurosaki *et al.* (2000) performed molecular dynamics calculations of the heat capacity of UN, and obtained a good agreement with the experimental results up to 1500 K, where the effects of lattice defects are marginal. Experimental high-temperature heat capacity data for the higher nitrides are scarce. The heat capacity of NpN has been measured by Nakajima and Arai (2003) by differential scanning calorimetry. The recommended high-temperature heat capacity functions are given in Table 19.35.

The actinide mononitrides vaporize to give An(g) and N_2(g) molecules, as has been demonstrated experimentally for ThN, UN, PuN, and NpN. The detailed mass spectrometric studies for UN have demonstrated also that the UN molecule occurs in the vapor phase, though its pressure is about three orders of magnitude lower than that of U(g). The decomposition temperatures under 1 bar nitrogen are 3053 K for UN, 2948 K for NpN, and 2843 K for PuN. Under nitrogen pressure, the mononitrides melt congruently: 3080 K at 2–3 bar N_2 for ThN (Rand, 1975), 3123 K at 2.5 bar N_2 for UN (Matsui and Ohse, 1987), 3103 K at 9.9 bar N_2 for NpN, and 3103 K at 5 bar N_2 for PuN (Lemire *et al.*, 2001). Th_3N_4 decomposes to ThN before melting.

19.11.2 Gaseous nitrides

The actinide mononitrides principally vaporize to give the gaseous elements, but molecular UN has been identified in the vapor as a minor species by mass spectrometry (Gingerich, 1969; Venugopal *et al.*, 1992). Molecular ThN, UN, and PuN species were also identified by infrared absorption spectroscopy in low-temperature inert-gas matrices (Ar) as reported by Green and Reedy (1976, 1978b, 1979). From these measurements the harmonic frequency ω_e and the first anharmonic correction coefficient were derived. Unlike the actinide monoxides, the experimental data for mononitrides do not show a regular decrease from ThN to PuN. The value for UN ($\omega_e = 1007.7$ cm^{-1}) is significantly higher than the values for ThN ($\omega_e = 941.9$ cm^{-1}) and PuN ($\omega_e = 861.8$ cm^{-1}). The reason for this is not clear. Overall the experimental data are insufficient to derive reliable thermodynamic properties.

19.11.3 Phosphides, arsenides, and antimonides

The thermodynamic data on phosphides, arsenides, and antimonides are restricted to the uranium compounds, some plutonium compounds and a single neptunium compound. They are summarized in Table 19.37, and have been

Table 19.37 *Thermodynamic properties of selected crystalline actinide chalcogenides; estimated values are given in italics.*

	C_p(298.15 K) (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
ThS		69.79 ± 0.33	–399.6 ± 4.2	a
Th_2S_3		*180 ± 17*	–1083.7 ± 12.6	a
Th_7S_{12}		*641 ± 59*	–4130 ± 146	a
ThS_2		96.2 ± 8.4	–628 ± 42	a
Th_2S_5		215 ± 17	–1272 ± 84	a
US	50.54 ± 0.08	77.99 ± 0.21	–320.9 ± 12.6	a,b
U_2S_3	133.7 ± 0.8	199.2 ± 1.7	–880 ± 67	a,b
U_3S_5		*291 ± 25*	–1431 ± 100	a,b
US_2	74.64 ± 0.13	110.42 ± 0.21	–520.4 ± 8.0	a,b
U_2S_5		*243 ± 25*		a,b
US_3	95.60 ± 0.25	138.49 ± 0.21	–539.6 ± 10.6	a,b
USe	54.81 ± 0.17	96.52 ± 0.21	–275.7 ± 14.6	a,b
USe_2 (α)	79.16 ± 0.17	134.98 ± 0.25	–427 ± 42	a,b
USe_3		*177 ± 17*	–452 ± 42	a,b
U_2Se_3		261.4 ± 1.7	*–711 ± 75*	a,b
U_3Se_4		*339 ± 38*	–983 ± 85	a,b
UTe		*112 ± 5*	–182 ± 11	a
UTe_3	117.2 ± 1.0	214.2 ± 1.7	*–284 ± 63*	a
U_3Te_4			–684 ± 142	a,b
PuS		*74 ± 5*	*–364 ± 38*	a
PuS_2		*107 ± 13*	*–529 ± 54*	a
Pu_2S_3		*188 ± 17*	*–987 ± 100*	a
PuSe	59.7 ± 1.2	92.1 ± 1.8		b
PuTe	73.1 ± 2.9	107.9 ± 4.3		b

[a] Grønvold *et al.* (1984).
[b] NEA-TDB (Grenthe *et al.*, 1990; Guillaumont *et al.*, 2003).

taken from the assessments by the NEA teams (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).

19.12 CHALCOGENIDES

19.12.1 Sulfides

The experimental thermodynamic data on the actinide sulfides are restricted to the compounds of thorium and uranium. Data for the other actinides, essentially neptunium and plutonium, are based on estimates. A thorough review of the thermodynamic properties of the actinide sulfides (and the selenides and tellurides) was made by Grønvold *et al.* (1984), after which little new information has become available. For these systems, compounds with a wide variety of S/An ratios have been reported: the solids AnS, An_3S_4, An_2S_3, An_7S_{12}, AnS_2, An_2S_5, and AnS_3, and the gases AnX and AnX_2. The thermodynamic data for the solid compounds are summarized in Table 19.37, which is essentially based on the analyses by Grønvold *et al.* (1984). The values in the NEA-TDB report on uranium are essentially revisions of this work and are adopted here. The entropies of the uranium sulfides are a linear function of the S/U ratio, as shown in Fig. 19.31, confirming the estimates for U_3S_5 and U_2S_5.

19.12.2 Selenides and tellurides

Very few data also exist for the selenides and tellurides, again mainly for uranium compounds. However, for this compound group some plutonium compounds have been reported. Low-temperature heat capacities of PuSe and

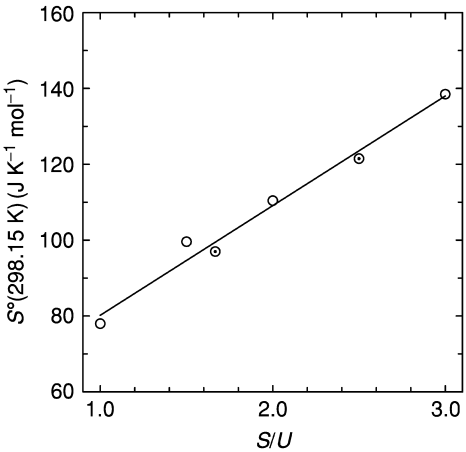

Fig. 19.31 *The entropies of the uranium sulfides (per mole of U) as a function of the S/U ratio; estimated values are indicated by* (⊙).

PuTe were measured by Hall *et al.* (1990, 1992) (see Table 19.37). No experimental determinations of the enthalpies of formation of these compounds exist.

19.13 OTHER BINARY COMPOUNDS

19.13.1 Compounds with group IIA elements

Thermodynamic data for binary compounds with group IIA elements are restricted to the actinide–beryllium systems. The compounds $ThBe_{13}$, UBe_{13}, and $PuBe_{13}$ have been characterized. A relatively complete data set is only available for UBe_{13} (see Tables 19.38 and 19.39) and have been assessed by the NEA team (Grenthe *et al.*, 1992). They include low-temperature heat capacity, enthalpy of formation and high-temperature heat capacity, and enthalpy increment measurements, the latter, however, in a limited temperature range (273–379 K). Unfortunately the high-temperature data are not consistent, and for this reason they give no recommendation. The value for the enthalpy of formation of $PuBe_{13}$ is taken from the assessment by Chiotti *et al.* (1981), and is based on an assessment of enthalpy of solution measurements.

19.13.2 Compounds with group IIIA elements

The systems of the actinides with group IIIA elements have significant technological relevance: the U–Al system for (materials testing) reactor fuel and the Pu–Ga for nuclear weapons. Also uranium borides have been considered for nuclear fuel materials. It is not surprising that these systems have been studied in more detail. Thermodynamic data for UB_2 are well established, and the high-temperature enthalpy increment measurement extend up to 2300 K. An anomalous increase of the heat capacity is observed (Fig. 19.32), as for many uranium compounds. The data have been assessed by Chiotti *et al.* (1981) and their selected values are included in Tables 19.38 and 19.39. For the U–Al compounds, only enthalpy of solution and EMF measurements have been made. However, Chiotti *et al.* (1981) do not give recommended values for the enthalpies of formation of the U–Al compounds. In Table 19.38 we have listed the values derived by Chiotti and Kately (1969), which are in good agreement with the other measurements. For the U–Ga system, Chiotti *et al.* (1981) cite only EMF and vapor pressure measurements and do not give thermodynamic values at 298.15 K. However, Palenzona and Cirafici (1975) measured the enthalpy of formation of UGa_3 and Prabhahara *et al.* (1998) measured the enthalpy of formation of UGa_3 and UGa_2 by solution calorimetry. Their results for UGa_3 are in poor agreement, but the results of Prabhahara *et al.* (1998) agree nicely with the EMF and vapor pressure studies. Their values are given in Table 19.38. In contrast, enthalpy of solution measurements are known for a number

Table 19.38 *Thermodynamic properties of other selected crystalline binary actinide compounds; estimated values are given in italics.*

	C_p(298.15 K) (J K^{-1} mol^{-1})	$S°$(298.15 K) (J K^{-1} mol^{-1})	$\Delta_f H°$(298.15 K) (kJ mol^{-1})	*References*
$ThSi_2$			–174.4	a
UBe_{13}	242.3 ± 4.2	180.1 ± 3.3	–163.6 ± 17.5	b
UB_2	55.35 ± 0.13	55.10 ± 0.13	–144.8 ± 12.6	a
UAl_2			–92.5 ± 8.4	a
UAl_3			–108.4 ± 8.4	a
UAl_4			–124.7 ± 8.4	a
UGa_3			–153.2 ± 17.6	c
UGa_2			–121.2 ± 18.0	c
USi_3			–132.2 ± 0.4	a
USi_2			–130.1 ± 1.3	a
USi			–80.3 ± 1.3	a
U_3Si_2			–170.3 ± 2.1	a
UGe_3		170.7	–106.7	a
UGe_2		130.5	–87.4	a
U_3Ge_5		351.9	–239.7	a
UGe		90.4	–61.5	a
U_5Ge_3		374.9	–23.1	a
UPd_3	102.10 ± 0.20	176.35 ± 0.30	–286 ± 22	d
URh_3	103.01 ± 0.20	152.24 ± 0.30	–302.0 ± 0.2	d,e
URu_3	101.42 ± 0.20	144.50 ± 0.29	–153.2 ± 0.2	d
$PuBe_{13}$			–149.4 ± 23.4	a
$PuAl_2$			–142.3 ± 10.0	a
$PuAl_3$ (hex)			–180.7 ± 10.0	a
$PuAl_4$ (α)			–180.7 ± 10.0	a
Pu_6Fe		425.6 ± 4.4	*–13.8 ± 4.6*	a
Pu_3Ga (β)			–158.2 ± 20.9	a
$PuGa_2$			–190.4 ± 31.4	a
$PuGa_6$			–238.1 ± 37.7	a
$PuSn_3$			–219.7 ± 11.3	a

[a] Chiotti *et al.* (1981).
[b] NEA-TDB (Grenthe *et al.*, 1992; Lemire *et al.*, 2001; Guillaumont *et al.*, 2003).
[c] Prabhahara *et al.* (1998).
[d] Cordfunke and Konings (1990).
[e] See text.

of compounds in the Pu–Ga system, and the assessed values by Chiotti *et al.* (1981) are included in Table 19.38.

19.13.3 Compounds with group IVA elements

The phase diagrams of the systems of the actinides with Si, Ge, Sn, and Pb have been studied in detail but thermodynamic data are scarce. Chiotti *et al.* (1981) did not give recommended values for the enthalpies of formation of any of the

Table 19.39 *High-temperature heat capacity of other crystalline actinide binary compounds;* $C_p/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a(T/\mathrm{K})^{-2} + b + c(T/\mathrm{K}) + d(T/\mathrm{K})^2 + e(T/\mathrm{K})^3$ (*estimated values are given in italics*).

	a (×10^{-6})	b	c (×10^{3})	d (×10^{6})	e (×10^{9})	T (K)	*References*
UB_2		16.0498	167.8	–131.52	36.553	2658	[a]
UPd_3	–0.28221	110.8964	–28.865	33.5733		1973	[b,c]
URu_3	–0.47184	101.224	18.46028			2123	[c]
URh_3	–0.61003	104.445	18.20548			2013	[c]

[a] Chiotti *et al*. (1981).
[b] See Fig. 19.32.
[c] Cordfunke and Konings (1990).

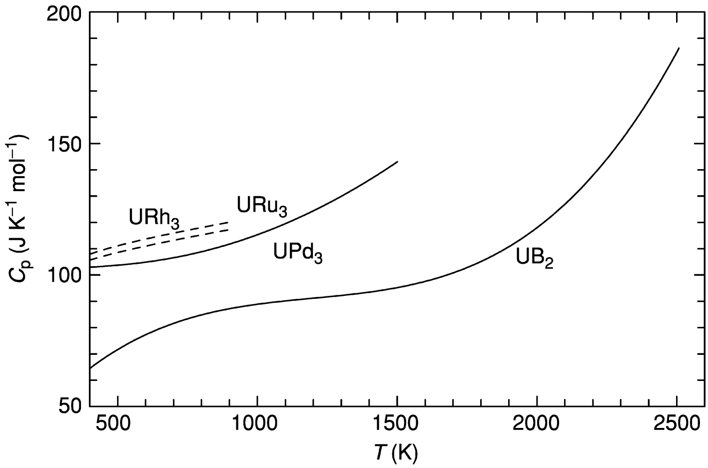

Fig. 19.32 *High-temperature heat capacity of some uranium intermetallic compounds. The UPd_3 curve is composed from the results of Burriel* et al. (1988) *and Arita* et al. (1997) *by scaling of the latter.*

compounds of these systems, except the U–Ge system. This is because there is often a distinct difference between the results from calorimetric (solution) measurements and EMF or vapor pressure measurement. However, measurement of the enthalpy of formation has been made that can be considered reliable. Robbins and Jenkins (1955) measured the enthalpy of formation of $ThSi_2$, Gross *et al.* (1962) measured the enthalpy of formation of USi_3, USi_2, USi, and U_3Si_2. For the U–Ge system, Chiotti *et al.* (1981) selected the values derived by Rand and Kubaschewski (1963) from vapor pressure measurements. These data are included Table 19.38.

19.13.4 Compounds with the transition elements (IB–VIIIB)

Chiotti *et al.* (1981) and Colinet and Pasturel (1994) discussed the thermodynamic data of the actinide intermetallic compounds with the transition metals in detail, Ward *et al.* (1986) the actinide–noble metal intermetallic compounds. The experimental basis for these compounds is limited and most of the work is done for the compounds of Th, U, and Pu.

(a) Enthalpies of formation

Extensive data exist for the systems An–Cd, An–Zn, and An–Bi that are of relevance to pyrochemical reprocessing, although the thermodynamic characterization of the compounds in these systems is limited. In most cases, only ΔG

functions at elevated temperatures have been reported, derived from EMF or vapor pressure measurements (see Chiotti *et al.*, 1981).

A large number of thermodynamic studies have been performed on the intermetallic compounds of uranium and the noble metals Ru, Rh, and Pd. The data were reviewed by Cordfunke and Konings (1990) and the recommended values are included in Table 19.38. The experimental EMF data on URu_3 and URh_3 reasonably agree, but a big discrepancy exists for UPd_3 for which a fluorine combustion study gave a much more negative value (-524 kJ mol^{-1}) than the value derived from vapor pressure measurements (-260 kJ mol^{-1}). Jung and Kleppa (1991) performed direct reaction calorimetry on these three compounds, and their result for UPd_3 $-(286 \pm 22)$ kJ mol^{-1} suggests that the fluorine combustion values are found to be in error. On the other hand, Prasad *et al.* (2000) reported a value close to the combustion value, derived from gas-equilibrium measurements. This example shows the difficulties determining accurate thermochemical data for these compounds.

Two semiempirical models are generally used to explain the trends and to estimate the unknown thermodynamic quantities of the actinide intermetallic compounds: the Engel–Brewer model and the Miedema model, as discussed extensively by Chiotti *et al.* (1981) and Ward *et al.* (1986). The Engel–Brewer model correlates thermodynamic properties with electronic structure. Brewer postulated that the s- and p-electrons involved in the bonding determine the crystal structure, whereas the d-electrons affect the chemical bonding and thermodynamic properties. The Engel–Brewer model is based on the promotion of atoms to valence states involving unpaired electrons suitable for bond formation with covalent character. The promotional energy to unpair the electrons was found to be 67 kJ mol^{-1} for the d^3s state in Th, 75 kJ mol^{-1} for the f^3d^2s state in U, and 180 kJ mol^{-1} for the f^5d^2s state in Pu (Brewer, 1970).

The Miedema model (de Boer *et al.*, 1988) correlates the enthalpy of formation of an intermetallic compound with the electronegativity and the electron density at the atomic cell boundary:

$$\Delta H = f(c)\left[-P(\Delta\phi^*)^2 + Q_0\left(\Delta n_{\mathrm{ws}}^{1/3}\right)^2\right] \tag{19.33}$$

where $f(c)$ is a function of the concentration of the metals, ϕ^* and Δn_{ws} the electronic work function of a pure metal and the electronic potential at the cell boundary, and P and Q_0 are constants. Fig. 19.33 shows the enthalpies of formation of actinide AnM_2 compounds with the 3d, 4d, and 5d transition elements predicted by this model (Ward *et al.*, 1986), indicating the limited stability of actinide compounds with the early d-transition elements (IVB, VB, and VIB) and a high stability of the compound with late d-transition elements. The Miedema model predicts $\Delta_f H^\circ(298.15\ \mathrm{K}) = -244$ kJ mol^{-1} for UPd_3 (de Boer *et al.*, 1988), which is close to the experimental values obtained by reaction calorimetry and vapor pressure measurements (see above). As concluded by Chiotti *et al.* (1981) after a systematic analysis of the thermodynamic

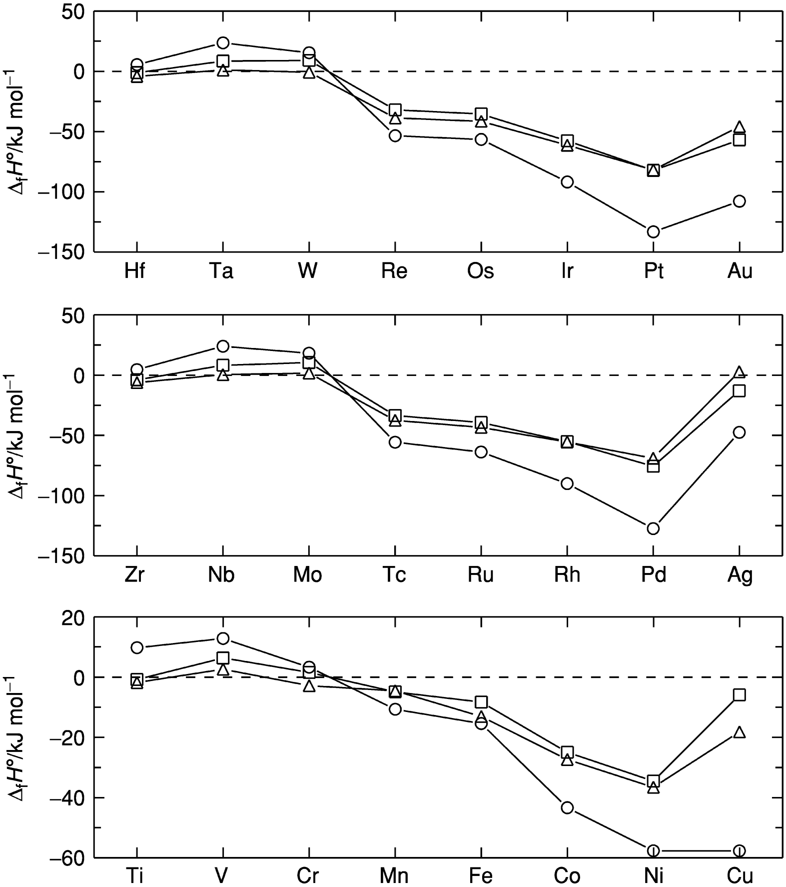

Fig. 19.33 *The enthalpies of formation predicted for actinide intermetallic phases AnM_2 from the Miedema correlation, as a function of the transition metal component,* (○) *Th,* (□) *U and* (Δ) *Pu* (*after Ward* et al., 1986).

data for intermetallic actinide compounds, estimates with Miedema's model are seldom in error by more than 20%, though it does not take into account the role of 5f electrons.

(b) Heat capacity and entropy

Accurate low-temperature (up to 300 K) heat capacity measurements have only been made for a limited number of uranium intermetallic compounds (URu_3, URh_3, and UPd_3). The derived entropy values at 298.15 K are given in Table 19.38. Also heat capacity measurements for some plutonium intermetallic compounds (Pu_6Fe) have been made, but of significantly less accuracy due to the small sample masses used. It should be noted, however, that low-temperature heat capacity measurements below 50 K have been made for many actinide intermetallic compounds, due to their interesting magnetic and superconducting properties. It can be noted here that the heat capacity data for UPd_3 confirm that the f-electrons in this compound are localized, leading to discrete energy levels, in contrast to URu_3 and URh_3, in which the f-electrons are itinerant.

Moriyama *et al.* (1990) proposed a correlation to estimate the entropies of intermetallic compounds based on the assumption that the (vibrational) entropy is proportional to the logarithm of the bond energy. The entropies of the MA_n compound and the elements M and A are described by:

$$S(\mathrm{MA}_n) = a\ln[\{E(\mathrm{M}) + nE(\mathrm{A}) - \Delta_\mathrm{f}H^\circ\}/(1+n)] + b_1 \tag{19.34}$$

$$S(\mathrm{M}) = a\ln E(\mathrm{M}) + b_2$$

$$S(\mathrm{A}) = a\ln E(\mathrm{A}) + b_3$$

where E is the bond energy of the metal, which was approximated by the sublimation enthalpy. The entropy of formation of the MA_n compound was then calculated from the equation:

$$\Delta_\mathrm{f}S(\mathrm{MA}_n) - a\ln H' + b' \tag{19.35}$$

with $H' = [\{E(\mathrm{M}) + nE(\mathrm{A}) - \Delta_\mathrm{f}H^\circ(\mathrm{MA}_n)\}/(1+n)]^{(1+n)}E(\mathrm{M})^{-1}E(\mathrm{A})^{-n}$. Indeed a linear relation was found for the actinide intermetallics considered. The coefficient a was determined empirically to be –61.9 J K^{-1} mol^{-1} and b was found to be zero, using known entropy values for actinide intermetallics.

(c) High-temperature properties

High-temperature heat capacities of only a limited number of intermetallic actinide compounds have been measured. Systematic studies have been made on the intermetallic compounds of uranium with the noble metals Rh, Ru, and Pd. Cordfunke *et al.* (1985) and Burriel *et al.* (1988) have reported enthalpy increment measurements for URh_3, URu_3, and UPd_3 and found excellent agreement with the low-temperature data. Arita *et al.* (1997) measured the heat capacity of UPd_3 but their results poorly agree with the enthalpy data of Burriel *et al.* (1988). However, their results indicate a rapid increase above 900 K (Fig. 19.32) that was attributed to lattice defect formation. The recommended heat capacity functions are summarized in Table 19.39. No data are known for the liquid phase of any of these compounds.

19.14 CONCLUDING REMARKS

The present chapter shows that a steady progress has been made in the determination and understanding of the thermodynamic properties of the actinide elements and compounds since the first edition of this work. Not only the number of compounds has been extended considerably, but also the quality of the data and the quality of the methods for estimation has improved considerably. In general it can be concluded that the systematics in the thermodynamic properties reflect the well-known change from itinerant f-electrons at the beginning of the actinide series to localized f-electrons from Am and beyond.

However, the overall quality of the thermodynamic data differs considerably between the various groups of compounds:

- The thermodynamic properties of the main actinide elements are fairly well established. Improvement is still needed for Ac, Pa, and the elements from Am onwards, but due to the high radioactivity of these elements and their limited availability, many additional measurements are not to be expected in the coming decades. But since the trends in the thermodynamic properties are reasonably well understood, the estimates presented here must be considered reliable.
- The thermodynamic data for actinide ions in aqueous solutions are still not satisfactory, even for the main actinides. Especially the values for the standard entropies of the aqueous species are based on few experiments and need improvement. The thermodynamic data of ions in molten salts have improved considerably for the LiCl–KCl (eutectic) but are still of poor quality for $LiF–BeF_2$. Other molten salt solvents have hardly been studied.
- The solid oxides (binary, ternary, quaternary) have been studied extensively and many systematics have been established. For this group there is a considerable mismatch between the large number of enthalpy of formation data and the limited number of entropy data. Also the high-temperature heat capacity data are limited. This is very apparent for the complex solid oxides. The data for the gaseous binary oxides are incomplete and require further studies: experimental studies to identify the molecular species and quantum chemical studies to estimate their properties.
- The actinide halides show the largest number of different oxidation states in both solid and gaseous state. Except for some technologically important halides (UF_6) the thermodynamic properties of this group are still surprisingly poorly characterized in spite of many studies, and for the solid dihalides, for example, no measurements exist at all. Trends and systematics in the AnX_n series and comparison to the LnX_3 and LnX_2 series, however, allow reasonable estimates, but there is still a need for experimental studies, especially heat capacity data at low and high temperatures.
- Relatively many studies of the dissociation pressures of the $An–H_2$ systems have been performed. However, the thermodynamic properties of only limited number of compounds can be derived from these data.
- The properties of the actinide hydroxides have hardly been studied, and the few experimental results (e.g. $Am(OH)_3$) are not consistent.

- The thermodynamic data for the carbides, pnictides, and chalcogenides are restricted to compounds of Th, U, and Pu. Because of their potential technological interest as nuclear fuels, the data are quite complete generally and extend up to high temperatures, though the available data on the gaseous molecules is scanty. The carbides, pnictides, and chalcogenides of other actinide have hardly been studied.
- Although the binary phase diagrams of actinides and other elements are generally well established, the basic thermodynamic data for alloys and intermetallic compounds are poorly known, even for technologically relevant systems. Predictive models have been developed, but the lack of reliable data makes it difficult to judge them. Moreover, the chemical bonding in actinide compounds is much more complex than in lanthanide or transition metal compounds, and possibly beyond the applicability of these models.

The need for further thermodynamic studies is thus as relevant as in the past decades. This is especially true because the trends in nuclear technology are moving in the direction of advanced nuclear systems for energy production with fuel cycles that include the proper treatment of plutonium and the minor actinides: fast reactors with innovative fuels, molten salt reactors, and advanced reprocessing (hydrochemical or pyrochemical). The development of these technologies demands better data for many actinide compounds, not only the pure substances but also their multicomponent mixtures, which have not been addressed in this chapter. To assure that such data will become available, the expertise in the field of actinide thermodynamics (both experimental and theoretical) must thus be maintained at a level that is needed for engineering, safety, and environmental applications, which is not evident now.

The data presented in this chapter are included in the f-MPD web-based material property information center of the Institute for Transuranium Elements (www.f-elements.net), from which complete thermodynamic tables can be retrieved. Corrections and updates will also be available from this site.

REFERENCES

Abraham, B. M., Brody, B. B., Davidson, N. R., Hagemann, F., Karle, I., Katz, J. J., and Wolf, M (1949) in *The Transuranium Element-Collected Papers* (eds. G. T. Seaborg, J. J. Katz, and W. M. Manning), McGraw-Hill, New York, pp. 740–58.

Ackermann, R. J., Faircloth, R. L., Rauh, E. G., and Thorn, R. J. (1966a) *J. Inorg. Nucl. Chem.*, **28**, 111–18.

Ackermann, R. J., Faircloth, R. L., and Rand, M. H. (1966b) *J. Phys. Chem.*, **70**, 3698–706.

Ackermann, R. J. and Rauh, E. G. (1973a) *Rev. Hautes Temp. Refract. Fr.*, **15**, 259–80.

Ackermann, R. J. and Rauh, E. G. (1973b) *High Temp. Sci.*, **5**, 462–73.

Ackermann, R. J. and Rauh, E. G. (1975) *J. Chem. Phys.*, **62**, 108–12.

Akabori, M., Kobayashi, F., Hayashi, H., Ogawa, T., Huntelaar, M. E., Booij, A. S., and Van Vlaanderen, P. (2002) *J. Chem. Thermodyn.*. **34**, 1461–6.

Ali, M., Mishra, R., Bharadwaj, S. R., Kerkar, A. S., Dharwadkar, S. R., and Das, D. (2001) *J. Nucl. Mater.*, **299**, 165–70.

Apelblatt, A. and Sahar, A. (1975) *JCS Faraday Trans. I*, **71**, 1667–70.

Archibong, E. F. and Ray, A. K. (2000) *J. Mol. Struct. (THEOCHEM)*, **530**, 165–70.

Arita, Y., Sasajima, N., and Matsui, T. (1997) *J. Nucl. Mater.*, **247**, 232–4.

Arkhipov, V. A., Gutina, E. A., Dobretsov, V. N., and Ustinov, V. A. (1974) *Sov. Radiochem.*, **16**, 122–4.

Bakker, K., Cordfunke, E. H. P., Konings, R. J. M., and Schram, R. P. C. (1997) *J. Nucl. Mater.*, **250**, 1–12.

Barin, I. and Knacke, O. (1973) *Thermochemical Properties of Inorganic Substances*, Springer Verlag, Berlin.

Barrett, S. A., Jacobson, A. J., Tofield, B. C., and Fender, B. E. F. (1982) *Acta Crystallogr.*, **B38**, 2775–8.

Bartscher, W. and Sari, C. (1986) *J. Nucl. Mater.*, **140**, 91–3.

Baes, C. F. Jr (1966) in *Thermodynamics*, vol. 1, IAEA, Vienna, pp. 409–33.

Baes, C. F. Jr (1969) in *Reprocessing of Nuclear Fuel*, Conf. 690–801; USAEC, p. 617.

Baes, C. F. Jr and Mesmer, R. E. (1976) *The Hydrolysis of Cations*, Wiley Interscience, New York.

Bazhanov, V. I., Ezhov, Yu. S., and Komarov, S. A. (1990a) *Zh. Strukt. Khim.*, **31**, 152–3.

Bazhanov, V. I., Komarov, S. A., Sevast'yanov, V. G., Popik, M., Kuznetsov, N. T., and Ezhov, Yu. S. (1990b) *Vysochist. Veshchestva*, **1**, 109–10.

Belov, A. N. and Semenov, G. A. (1980) *Zh. Fiz. Khim.*, **54**, 1537–41.

Belyaev, Yu. I., Smirnov, N. L., and Taranov, A. P. (1979) *Radiokhimiya*, **21**, 682–6.

Besmann, T. M. and Lindemer, T. B. (1983) *J. Am. Ceram. Soc.*, **66**, 782–5.

Besmann, T. M. and Lindemer, T. B. (1985) *J. Nucl. Mater.*, **130**, 489–504.

Besmann, T. M. and Lindemer, T. B. (1986) *J. Nucl. Mater.*, **137**, 292–3.

Bradbury, M. H. (1981) *J. Less Common Metals*, **78**, 207–18.

Brewer, L. (1970) *Plutonium 1970 and Other Actinides*, Nucl. Met. Ser. (AIME), **17**, 650.

Brewer, L. (1984) *High Temp. Sci.*, **17**, 1–30.

Brickwedde, F. G., Hodge, H. J., and Scott, R. B. (1948) *J. Chem. Phys.*, **16**, 429–36.

Brickwedde, F. G., Hodge, H. J., and Scott, R. B. (1951) in *The Chemistry of Uranium* (eds. J. J. Katz and E. Rabinowitch), Dover Publications, New York.

Brooks, M. S. S., Johnson, B., and Skriver, H. L. (1984) in *Handbook on the Chemistry and Physics of the Actinides* (eds. A. J. Freeman and G. L. Lander), North-Holland, Amsterdam, pp. 153–270.

Burnett, J. L. (1966) *J. Inorg. Nucl. Chem.*, **28**, 2454–6.

Burns, J. B., Haire, R. G., and Peterson, J. R. (1998) *J. Alloys Compds*, **271–273**, 676–9.

Burriel, R., To, M., Zaniel, H., Westrum, E. F. Jr, Cordfunke, E. H. P., Muis, R. P., and Wijbenga, G. (1988) *J. Chem. Thermodyn.*, **20**, 815–23.

Campbell, A. B. and Lemire, R. J. (1994) Atomic Energy of Canada Limited Report RC-1278, COG-I-94–399.

Casalta, S. (1996) Etude des proprietes du systeme Am-O en vue de la transmutation de l'americium 241 en reacteur a neutrons rapides, Ph.D. Thesis, University Aix-Marseille I.

Chereau, P., Dean, G., De Franco, M., and Gerdanian, P. (1977) *J. Chem. Thermodyn.*, **9**, 211–19.

Chevalier, P.-Y., Fischer, E., and Cheynet, B. (2000) *J. Nucl. Mater.*, **280**, 136–50.

Chikalla, T. D. and Eyring, L. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2281–93.

Chiotti, P. and Kately, J. A. (1969) *J. Nucl. Mater.*, **32**, 135–42.

Chiotti, P., Akhachinskij, V. V., Ansara, I., and Rand, M. H. (1981) The chemical thermodynamics of actinide elements and compounds, part 5, *The Actinide Binary Alloys*, STI/PUB/424/5, International Atomic Energy Agency, Vienna.

Cleveland, J. M. (1979) in *Chemical Modeling in Aqueous Systems* (ed. E. A. Jenne), (Am. Chem. Soc. Symp. Ser. 93), Washington, DC, pp. 321–38.

Colinet, C. and Pasturel, A. (1994) in *Handbook on the Chemistry of Rare Earths* (eds. K. A. Gschneidner Jr, L. Eyring, G. H. Lander and G. R. Choppin), vol. 19, ch. 134.

Conway, J. B. and Flagella, P. N. (1969) Report GEMP-1012, p. 61.

Cordfunke, E. H. P. (1964) *J. Phys. Chem.*, **68**, 3353–6.

Cordfunke, E. H. P. and O'Hare, P. A. G. (1978) The chemical thermodynamics of actinide elements and compounds, part 3, *Miscellaneous Actinide Compounds*, STI/PUB/424/3, International Atomic Energy Agency, Vienna.

Cordfunke, E. H. P., Muis, R. P., and Prins, G. (1979) *J. Chem. Thermodyn.*, **11**, 819–23.

Cordfunke, E. H. P. and Ouweltjes, W. (1981) *J. Chem. Thermodyn.*, **13**, 193–7.

Cordfunke, E. H. P., Ouweltjes, W., and Prins, G. (1982) *J. Chem. Thermodyn.*, **14**, 495–502.

Cordfunke, E. H. P., Muis, R. P., Ouweltjes, W., Flotow, H. E., and O'Hare, P. A.G. (1982) *J. Chem. Thermodyn.*, **14**, 313–22.

Cordfunke, E. H. P. and Kubaschewski, O. (1984) *Thermochim. Acta*, **74**, 235–45.

Cordfunke, E. H. P., Muis, R. P., Wijbenga, G., Burriel, R., To, M., Zaniel, H., and Westrum, E. F. Jr (1985) *J. Chem. Thermodyn.*, **17**, 1035–44.

Cordfunke, E. H. P., Konings, R. J. M., and Westrum, E. F. Jr (1989) *J. Nucl. Mater.*, **167**, 205–12.

Cordfunke, E. H. P. and Konings, R. J. M. (1990) *Thermochemical Data for Reactor Materials and Fission Products*, Elsevier, Amsterdam.

Cordfunke, E. H. P. and IJdo, D. J. W. (1994) *J. Solid State Chem.*, **109**, 272–6.

Cordfunke, E. H. P., Booij, A. S., Smit-Groen, V. S., van Vlaanderen, P., and Ijdo, D. J. W. (1997) *J. Solid State Chem.*, **131**, 341–9.

Cordfunke, E. H. P., Booij, A. S., and Huntelaar, M. E. (1999) *J. Chem. Thermodyn.*, **31**, 1337–45.

Cordfunke, E. H. P. and Konings, R. J. M. (2001a) *Thermochim. Acta*, **375**, 17–50.

Cordfunke, E. H. P. and Konings, R. J. M. (2001b) *Thermochim. Acta*, **375**, 51–64.

Cordfunke, E. H. P. and Konings, R. J. M. (2001c) *Thermochim. Acta*, **375**, 65–79.

Cox, J. D., Wagman, D. D., and Medvedev, V. A. (1989) *CODATA Key Values for Thermodynamics*, Hemisphere, New York.

Criss, C. M. and Cobble, R. W. (1964) *J. Am. Chem. Soc.*, **86**, 5385–9.

Dash, S., Singh, Z., Prasad, R., and Venugopal, V. (2000) *J. Nucl. Mater.*, **279**, 84–90.

David, F., Samhoun, K., Guillaumont, R., and Edelstein, N. (1978) *J. Inorg. Nucl. Chem.*, **40**, 69–74.

David, F. (1986) in *Handbook on the Chemistry of the Actinides* (eds. A. J. Freeman and C. Keller), vol. 4, ch. 3.

David, F. H. and Vokhmin, V. (2001) *J. Phys. Chem. A*, **105**, 9704–9.
David, F. H., Vokhmin, V., and Ionova, G. (2001) *J. Mol. Liquids*, **90**, 45–62.
David, F. H. and Vokhmin, V. (2002) *J. Nucl. Sci. Technol.*, Suppl. 3, 286–9.
De Boer, F. R., Boom, R., Matthens, W. C. M., and Miedema, A. R. (1988) *Cohesion in Metals*, Elsevier, Amsterdam.
Dharwadkar, S. R., Tripathi, S. N., Karkhana, M. D., and Chandrasekharaiah, M. S. (1975) in *Proc. Symp. on Thermodynamics of Nuclear Materials 1974*, IAEA, Vienna, vol. II, pp. 455–65.
Diakonov, I. I., Tagirov, B. R., and Ragnarsdottir, K. V. (1998a) *Radiochim. Acta*, **81**, 107–16.
Diakonov, I. I., Tagirov, B. R., and Ragnarsdottir, K. V. (1998b) *Chem. Geol.*, **151**, 327–47.
Ebbinghaus, B. B. (1995) Report UCRL-JC-122278, Lawrence Livermore National Laboratory.
Evans, J. H. and Mardon, P. G. (1959) *J. Phys. Chem. Solids*, **10**, 311–18.
Felmy, A. R., Rai, D., Schramke, J. A., and Ryan, J. L. (1989) *Radiochim. Acta*, **48**, 29–35.
Finch, R. J., Hawthorne, F. C., and Ewing, R. C. (1998) *Can. Miner.*, **36**, 831–45.
Fink, J. K. (1982) *Int. J. Thermophys.*, **3**, 165–200.
Fink, J. K. (2000) *J. Nucl. Mater.*, **279**, 1–18.
Flotow, H. E. and Tetenbaum, M. (1981) *J. Chem. Phys.*, **74**, 5269–77.
Flotow, H. E., Haschke, J. M., and Yamauchi, S. (1984) The chemical thermodynamics of actinide elements and compounds, Part 9, *The Actinide Hydrides*, STI/PUB/424/9, International Atomic Energy Agency, Vienna.
Foster, K. W. (1953) Report MLM-901.
Fournier, J. M. (1976) *J. Phys. Chem. Solids*, **37**, 235–44.
Fuger, J., Brown, D., and Easey, J. F. (1969) *J. Chem. Soc. A*, 2995–8.
Fuger, J. and Brown, D. (1975) *J. Chem. Soc., Dalton Trans.*, 225–31.
Fuger, J. and Oetting, F. L. (1976) The chemical thermodynamics of actinide elements and compounds, part 2, *The Actinide Aqueous Ions*, STI/PUB/424/2, International Atomic Energy Agency, Vienna.
Fuger, J., Bohet, J., Müller, W., Whittacker, B., and Brown, D. (1978) *Inorg. Nucl. Chem. Lett.*, **14**, 11–18.
Fuger, J., Haire, R. G., and Peterson, J. R. (1981) *J. Inorg. Nucl. Chem.*, **43**, 3209–15.
Fuger, J., Parker, V. B., Hubbard, W. N., and Oetting, F. L. (1983) The chemical thermodynamics of actinide elements and compounds, part 8, *The Actinide Halides*, STI/PUB/424/8, International Atomic Energy Agency, Vienna.
Fuger, J., Haire, R. G., and Peterson, J. R. (1984) *J. Less Common Metals*, **98**, 315–21.
Fuger, J., Haire, R. G., Wilmarth, W. R., and Peterson, J. R. (1990) *J. Less Common Metals*, **158**, 99–104.
Fuger, J., Khodakovsky, I. L., Sergeyeva, E. I., Medvedev, V. A., and Navratil, J. D. (1992) The chemical thermodynamics of actinide elements and compounds, part 12, *The Actinide Aqueous Inorganic Complexes*, STI/PUB/424/12, International Atomic Energy Agency, Vienna.
Fuger, J., Haire, R. G., and Peterson, J. R. (1993) *J. Alloys Compds*, **200**, 181–5.
Fusselman, S. P., Roy, J. J., Grimmet, D. L., Grantham, L. F., Krueger, C. L., Nabalek, C. R., Storvick, T. S., Inoue, T., Hijikata, T., Kinoshita, K., Sakamura, Y., Uozumi, K., Kawai, T., and Takahashi, N. (1999) *J. Electrochem. Soc.*, **146**, 2573–80.

Gabelnick, S. D., Reedy, G. T., and Chasanov, M. G. (1974) *J. Chem. Phys.*, **60**, 1167.

Gibby, R. L., McNeilly, C. E., and Chikalla, T. D. (1970) *J. Nucl. Mater.*, **34**, 299–306.

Gibson, J. K. and Haire, R. G. (1988a) *Thermochim. Acta.*, **133**, 241–7.

Gibson, J. K. and Haire, R. G. (1988b) *J. Solid State Chem.*, **73**, 524.

Gibson, J. K. and Haire, R. G. (1990) *J. Phys. Chem.*, **94**, 935.

Gibson, J. K. and Haire, R. G. (1992) *J. Nucl. Mater.*, **195**, 156–65.

Gibson, J. K. (2003) *J. Phys. Chem. A*, **107**, 7891–9.

Gingerich, K. A. (1969) *J. Chem. Phys.*, **67**, 4433.

Glushko, V. P., Medvedev, V. A., Bergman, G. A., Gurvich, L. V., Vorob'ev, A. F., Vasil'ev, V. P., Kolesov, V. P., Yungman, V. S., Reznutskij, L. R., Baibuz, V. F., Gal'chenko, G. L., and Yatzimirskij, K. B. (1978) *Thermodynamic Constants Of Substances*, Academy of Science Publishing House, Moscow.

Gorokhov, L. N., Smirnov, V. K., and Khodeev, Yu. S. (1984) *Russ. J. Phys. Chem.*, **58**, 980–7.

Gorokhov, L. N. and Sidorova, I. V. (1998) *Russ. J. Phys. Chem.*, **72**, 1038–42.

Goudiakas, J., Haire, R. G., and Fuger, J. (1990) *J. Chem. Thermodyn.*, **22**, 577–87.

Green, D. W. and Reedy, G. T. (1976) *J. Chem. Phys.*, **65**, 2921–7.

Green, D. W. and Reedy, G. T. (1978a) *J. Chem. Phys.*, **69**, 544–51.

Green, D. W. and Reedy, G. T. (1978b) *J. Chem. Phys.*, **69**, 552–5.

Green, D. W. and Reedy, G. T. (1979) *J. Mol. Spectrosc.*, **74**, 423–34.

Green, D. W. (1980) *Int. J. Thermophys.*, **1**, 61.

Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, Cregu, C., and Wanner, H. (1992) *Chemical Thermodynamics of Uranium* (eds. H. Wanner and I. Forest), North Holland, Amsterdam.

Grønvold, F., Drowart, J., and Westrum, E. F. Jr (1984) The chemical thermodynamics of actinide elements and compounds, part 4, *The Actinide Chalcogenides (Excluding Oxides)*, STI/PUB/424/4, International Atomic Energy Agency, Vienna.

Gross, P., Hayman, C., and Clayton, H. (1962) in *Proc. Thermodyn. Nucl. Mater.*, IAEA, Vienna, pp. 653–65.

Gross, P., Hayman, C., and Wilson, G. L. (1971) *Monathsh. Chem.*, **102**, 924–8.

Gruen, D. M. and DeKock, C. W. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2569.

Gruen, D. M. (1976) *Proc. Int. Symp. Molten Salts*, Washington, DC, p. 204.

Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D., and Rand, M. H. (2003) *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, Elsevier, Amsterdam.

Gupta, S. K. and Gingerich, K. A. (1979) *J. Chem. Phys.*, **71**, 3072.

Gupta, S. K. and Gingerich, K. A. (1980) *J. Chem. Phys.*, **72**, 2795.

Haaland, A., Martinsen, K.-G., Swang, O., Volden, H., Booij, A. S., and Konings, R. J. M. (1995) *J. Chem. Soc., Dalton Trans.*, 185–90.

Haire, R. G. and Gibson, J. K. (1989) *J. Chem. Phys.*, **91**, 7085–96.

Haire, R. G. (1994) *J. Alloys Compds*, **213/214**, 185–91.

Haire, R. G. and Eyring, L. (1994) Comparisons of the binary oxides, in *Handbook of the Rare Earths,* vol. 18 (eds. K. A. Gschneidner, L. Eyring, G. H. Lander, and G. R. Choppin), North-Holland, Amsterdam, 18: 413.

Hall, R. O. A., Jeffery, A. J., Mortimer, M., and Spirlet, J. C. (1990) Report AERE-R-13490.

Hall, R. O. A., Mortimer, M., Harding, S. R., and Spirlet, J. C. (1992) Report AEA-FS-0048H.

Hall, R. O. A., Mortimer, M., and Spirlet, J. C. (1990) Report AERE-R-13768.
Han, Y.-K. (2001) *J. Comp. Chem.*, **22**, 2010–221.
Haschke, J. M., Allen, T. H., and Morales, L. A. (2001) *J. Alloys Compds*, **314**, 78–84.
Haschke, J. M. and Allen, T. H. (2002) *J. Alloys Compds*, **336**, 124–30.
Hayes, S. L., Thomas, J. K., and Pedicord, K. L. (1990) *J. Nucl. Mater.*, **171**, 300–18.
Helean, K. B., Navrotsky, A., Vance, E. R., Carter, M. L., Ebbinghaus, B., Krikorian, O., Lian, J., Wang, L. M., and Catalano, J. G. (2002) *J. Nucl. Mater.*, **303**, 226–39.
Helean, K. B., Navrotsky, A., Lumpkin, G. R., Colella, M., Lian, J., Ewing, R. C., Ebbinghaus, B., and Catalano, J. G. (2003) *J. Nucl. Mater.*, **320**, 231–44.
Hiernaut, J. P., Hyland, G. J., and Ronchi, C. (1993) *Int. J. Thermophys.*, **14**, 609–18.
Hiernaut, J. P. and Ronchi, R. (2004) *J. Nucl. Mater.*, **334**, 133–8.
Hildenbrand, D. L., Gurvich, L. V., and Yungman, V. S. (1985) The chemical thermodynamics of actinide elements and compounds, part 13, *The Gaseous Actinide Ions*, STI/PUB/424/13, International Atomic Energy Agency, Vienna.
Hildenbrand, D. L. (1988) *Pure Appl. Chem.*, **60**, 303–10.
Hildenbrand, D. L. and Lau, K. H. (1990) *J. Chem. Phys.*, **90**, 5983.
Hildenbrand, D. L. and Lau, K. H. (1991) *J. Chem. Phys.*, **94**, 1420.
Hobart, D. E., Samhoun, K., and Peterson, J. R. (1982) *Radiochim. Acta*, **31**, 139.
Hobart, D. E., Varlashkin, P. G., Samhoun, K., Haire, R. G., and Peterson, J. R. (1983) *Rev. Chim. Miner.*, **20**, 817–27.
Holley, C. E., Rand, M. H., and Storms, E. K. (1984) The chemical thermodynamics of actinide elements and compounds, part 6, *The Actinide Carbides*, STI/PUB/424/6, International Atomic Energy Agency, Vienna.
Hovey, J. K. and Tremaine, P. R. (1986) *Geochim. Cosmochim. Acta*, **50**, 453.
Hovey, J. K., Nguyen-Trung, C., and Tremaine, P. R. (1989) *Geochim. Cosmochim. Acta*, **53**, 1503–9.
Hovey, J. K. (1997) *J. Phys. Chem. B*, **101**, 4321.
Huang, J., Yamawaki, M., Yamaguchi, K., Yasumoto, M., Sakurai, H., and Suzuki, Y. (1997a) *J. Nucl. Mater.*, **247**, 17–20.
Huang, J., Yamawaki, M., Yamaguchi, K., Yasumoto, M, Sakurai, H., and Suzuki, Y. (1997b) *J. Nucl. Mater.*, **248**, 257–61.
Hubener, S. and Zvara, I. (1982) *Radiochim. Acta*, **31**, 89–94.
Hughes-Kubatko, K.-A., Helean, K. B., Navrotsky, A., and Burns, P. C. (2003) *Science*, **302**, 1191–3.
Hultgren, R., Desai, P. D., Hawkins, D. T., Gleiser, M., Kelley, K. K., and Wagman, D. D. (1973) *Selected Values of the Thermodynamic Properties of the Elements*, American Society for Metals, Metals Park, Ohio.
Huntelaar, M. E., Booij, A. S., Ijdo, D., van Genderen, A., Akabori, M., Gaune- Escard, M., and Rycerz, L. (2002) *J. Nucl. Sci. Technol.*, Suppl. 3, 599–602.
IAEA (1965) *Thermodynamic and Transport Properties of Uranium Dioxide and Related Phases*, Technical Reports Series no. 39, International Atomic Energy Agency, Vienna.
IAEA (1967) *The Plutonium-Oxygen and Uranium-Plutonium-Oxygen Systems: A Thermochemical Assessment*, Technical Reports Series no. 79, International Atomic Energy Agency, Vienna.
Johnson, G. K. (1979) *J. Chem. Thermodyn.*, **11**, 483–9.
Johnson, G. K. (1985) *J. Nucl. Mater.*, **130**, 102–8.

Johnson, I. (1975) Report ANL-RDP-26.

Jones, L. H. and Ekberg, S. (1977) *J. Chem. Phys.*, **67**, 2591–8.

Joubert, L. and Maldivi, P. (2001) *J. Phys. Chem. A*, **105**, 9068–76.

Jung, W.-G. and Kleppa, O. J. (1991) *J. Chem. Thermodyn.*, **23**, 147.

Katz, J. J. and Rabinowitch, E. (1951) *The Chemistry of Uranium*, McGraw-Hill, New York.

Kaufman, M. J., Muenter, J., and Klemperer, W. (1967) *J. Chem. Phys.*, **47**, 3365–70.

Kim, K. C. and Mulford, R. N. (1990) *J. Mol. Struct. (THEOCHEM)*, **207**, 293.

Kleinschmidt, P. D., Ward, J. W., and Haire, R. G. (1983) *Proc. II Symp. on High Temperature Materials Chemistry* (eds. Z. Munir and D. Cubiciotti), Electrochemical Society, Pennington, NJ, pp. 23–31.

Kleinschmidt, P. D., Ward, J. W., and Haire, R. G. (1984) *J. Phys. Chem.*, **81**, 473.

Kleinschmidt, P. D., and Ward, J. W. (1986) *J. Less Common Metals*, **121**, 61.

Kleinschmidt, P. D. (1988) *J. Chem. Phys.*, **89**, 6897.

Konings, R. J. M., Booij, A. S., Kovács, A., Girichev, G. V., Giricheva, N. I., and Krasnova, O. G. (1996) *J. Mol. Struct.*, **378**, 121–31.

Konings, R. J. M. and Hildenbrand, D. L. (1998) *J. Alloys Compds*, **271–273**, 583–6.

Konings, R. J. M. (2001a) *J. Nucl. Mater.*, **295**, 57–63.

Konings, R. J. M. (2001b) *J. Nucl. Mater.*, **298**, 255–68.

Konings, R. J. M. (2002) *J. Nucl. Mater.*, **301**, 223–6.

Konings, R. J. M. (2003) *J. Alloys Compds*, **348**, 38–42.

Konings, R. J. M. and Kovács, A. (2003) in *Handbook on the Physics and Chemistry of Rare Earths*, vol. 33, ch. 213 (eds. K. A. Gschneidner Jr and J.-C. G. Bünzli, and V. K. Pecharsky) Elsevier, pp. 147–247.

Konings, R. J. M. (2004a) *J. Chem. Thermodyn.*, **36**, 121–6.

Konings, R. J. M. (2004b) www.f-elements.net.

Konings, R. J. M., van Miltenburg, J. C., and van Genderen, A. G. C. (2005) *J. Chem. Thermodyn.*, **37** (2005), 1219–25.

Kosyakov, V. N., Timofeev, G. A., Erin, I. A., Kopytov, V. V., and Andreev, V. J. (1977) *Radiokhimiya*, **19**, 82.

Kovács, A., Booij, A. S., Cordfunke, E. H. P., Kok-Scheele, A., and Konings, R. J. M. (1996) *J. Alloys Compds*, **241**, 95–7.

Kovács, A., Konings, R. J. M., and Nemcsok, D. S. (2003) *J. Alloys Compds*, **353**, 128–32.

Krestov, G. A. (1972) *Thermochemistry of Compounds of Rare-Earth and Actinide Elements*, Atomizdat, Moscow (English translation, AEC-tr-7505, National Technical Information Service, Springfield, VA 22151).

Krikorian, O. H., Ebbinghaus, B. B., Adamson, M. G., Fontes, A. S. Jr, and Fleming, D. L. (1993a) Report UCRL-ID-112994.

Krikorian, O. H., Condit, R. H., Fontes, A. S. Jr, Fleming, D. L., Magana, J. W., Morris, W. F., and Adamason, M. G. (1993b) Report UCRL-ID-114774.

Krupa, J. C. and Gajek, Z. (1991) *Eur. J. Solid State Chem.*, **28**, 143.

Krupa, J. C. (2001) personal communication to R. J. M. Konings.

Küchle, W., Dolg, M., Stoll, H., and Preus, H. (1994) *J. Chem. Phys.*, **100**, 7535.

Kunze, K. R., Hauge, R. H., Hamill, D., and Margrave, J. L. (1976) *J. Chem. Phys.* **65**, 2026.

Kurosaki, K., Yano, K., Yamada, K., Uno, M., and Yamanaka, S. (2000) *J. Alloys Compds*, **297**, 1.

Kuznietz, M. (1968) *J. Chem. Phys.*, **49**, 3731.

Lambertin, D., Lacquement, J., Sanchez, S., and Picard, G. S. (2000) *Plasmas and Ions*, **3**, 65.

Larson, D. T. and Haschke, J. M. (1981) *Inorg. Chem.*, **20**, 1945–50.

Latimer, W. M. (1952) *Oxidation Potentials*, 2nd edn, Prentice-Hall, New York.

Lau, K. H. and Hildenbrand, D. L. (1982) *J. Chem. Phys.*, **76**, 2646.

Lau, K. H. and Hildenbrand, D. L. (1984) *J. Chem. Phys.*, **80**, 1312.

Lau, K. H. and Hildenbrand, D. L. (1987) *J. Chem. Phys.*, **86**: 2949.

Lau, K. H. and Hildenbrand, D. L. (1990) *J. Chem. Phys.*, **92**: 6124–6130.

Lau, K. H., Brittain, R. D., and Hildenbrand, D. L. (1989) *J. Chem. Phys.*, **90**, 1158.

Lau, K. H., and Hildenbrand, D. L., (1989) *J. Chem. Phys.*, **90**, 1158.

Lebedev, L. A. (1981) *Radiokhimiya*, **23**, 12.

Lemire, R. J. and Tremaine, P. R. (1980) *J. Chem. Eng. Data*, **25**, 361–70.

Lemire, R. J. (1984) Atomic Energy of Canada Ltd Report AECL-7817, Whiteshell Nuclear Research Establishment.

Lemire, R. J., Campbell, A. B., Saluja, P. P. S., and Le Blanc, J. C. (1993) *J. Nucl. Mater.*, **201**, 165–75.

Lemire, R. J. and Campbell, A. B. (1996a) *Radiochim. Acta*, **73**, 131–7.

Lemire, R. J. and Campbell, A. B. (1996b) *Thermochim. Acta*, **286**, 225–31.

Lemire, R. J., Fuger, J., Nitsche, H., Potter, P., Rand, M. H., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., and Wanner, H. (2001) *Chemical Thermodynamics of Neptunium and Plutonium*, Elsevier, Amsterdam.

Libowitz, G. G. and Maeland, A. J. (1979) in *Handbook on Physics and Chemistry of Rare Earths* (eds. L. R. Eyring and K. A. Gschneidner Jr), vol. 3, pp. 299–336.

Lindemer, T. B., Besmann, T. M., and Johnson, C. E. (1981) *J. Nucl. Mater.*, **100**, 178–226.

Lindemer, T. B. and Besmann, T. M. (1985) *J. Nucl. Mater.*, **130**, 473–88.

Linevsky (1963) General Electric Report WADD-TR-60-646.

Malm, J. G., Williams, C. W., Soderholm, L., and Morss, L. R. (1993) *J. Alloys Compds*, **194**, 133.

Maly, J. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 373.

Maly, J. and Cunningham, B. B. (1967) *Inorg. Nucl. Chem. Lett.*, **3**, 445.

Maly, J., Sikkeland, T., Silva, R., and Ghiorso, A. (1968) *Science*, **160**, 1114–15.

Martinot, L. (1978) *Encyclopedia of Electrochemistry of the Elements*, vol. VIII (ed. A. J. Bard), Marcel Dekker, New York, pp. 149–206.

Martinot, L. (1982) in *Handbook on the Physics and Chemistry of the Actinides* (eds. A. J. Freeman and C. Keller), vol. 6, ch. 4, North-Holland, Amsterdam, p. 241.

Martinot, L., and Fuger, J. (1985) *Standard Potentials in Aqueous Solutions* (eds. A. J. Bard, R. Parsons, and J. Jordan), Marcel Dekker, New York. ch. 21.

Matsuda, T., Yamanaka, S., Kurosaki, K., Uno, M., and Kobayashi, S. (2001) *J. Alloys Compds*, **322**, 77.

Matsui, T., and Ohse, R. W. (1987) *High Temp.–High Press.*, **19**, 1–17 (see also Report EUR 10858 EN).

Mazeina, L., Ushakov, S. V., Navrotsky, A., and Boatner, L. A. (2005) *Geochim. Cosmochim. Acta*, **69**, 4675–83.

Merli, L. and Fuger, J. (1994) *Radiochim. Acta*, **66/67**, 109–13.
Merli, L., Lambert, B., and Fuger, J. (1997) *J. Nucl. Mater.*, **247**, 172–6.
Mikheev, N. B. (1983) *Radiochim. Acta*, **32**, 69.
Molnar, J. and Hargittai, M. (1995) *J. Phys. Chem.*, **99**, 10780.
Moriyama, H., Konoshita, K., and Ito, Y. (1990) *J. Nucl. Sci. Technol.*, **27**, 827–34.
Morss, L. R. (1976) *Chem. Rev.*, **76**, 827–41.
Morss, L. R. and Fahey, J. A. (1976) *Proc. 12th Rare Earth Res. Conf.*, vol. 1, Denver Research Institute, Denver, CO, pp. 443–50.
Morss, L. R. and McCue, M. C. (1976) *J. Chem. Eng. Data*, **21**, 337–41.
Morss, L. R. and Fuger, J. (1981) *J. Inorg. Nucl. Chem.*, **43**, 2059–64.
Morss, L. R. (1983) *J. Less Common Metals*, **93**, 301–21.
Morss, L. R. (1985) in *Americium and Curium Chemistry and Technology* (ed. N. Edelstein), D. Reidel, Dordrecht, The Netherlands, pp. 147–58.
Morss, L. R. and Sonnenberger, D. C. (1985) *J. Nucl. Mater.*, **130**, 266–72.
Morss, L. R., Fuger, J., Goffart, J., Edelstein, N., Shalimoff, G. V. (1987) *J. Less Common Metals*, **127**, 251.
Morss, L. R. and Eller, P. G. (1989) *Radiochim. Acta*, **47**, 51–4.
Morss, L. R. and Hall, J. P. (1994) *49th Annual Calorimetry Conference*, Santa Fe, NM, July 31–Aug 5, paper No. 63.
Morss, L. R. and Williams, C. W. (1994) *Radiochim. Acta*, **66/67**, 89–93.
Murad, E. and Hildenbrand, D. L. (1980) *J. Chem. Phys.*, **73**, 4005–11.
Musikas, C., Couffin, F., and Marteau, M. (1974) *J. Chim. Phys. Phys.-Chim. Biol.*, **5**, 641–8.
Nakajima, K., Arai, Y., and Suzuki, Y. (1997) *J. Nucl. Mater.*, **247**, 33–6.
Nakajima, K., Arai, Y., and Suzuki, Y. (1999a) *J. Nucl. Mater.*, **275**, 332–5.
Nakajima, K., Arai, Y., Suzuki, Y., and Yamawaki, M. (1999b) *J. Mass Spectrom. Soc. Jpn*, **47**, 46–8.
Nakajima, K. and Arai, Y. (2003) *J. Nucl. Sci. Technol.*, Suppl. 3, 620–623.
Newton, T. W. and Sullivan, J. C. (1985) in *Handbook on the Chemistry of the Actinides*, vol. 3 (eds. A. J. Freeman, G. L. Lander, and C. Keller), pp. 387–406.
Nugent, L. J., Burnett, J. L., and Morss, L. R. (1973) *J. Chem. Thermodyn.*, **5**, 665–72.
Oetting, F. L. (1967) *Chem. Rev.*, **67**, 261–97.
Oetting, F. L., Rand, M. H., and Ackermann, R. J. (1976) The chemical thermodynamics of actinide elements and compounds, part 1, *The Actinide Elements*, STI/PUB/424/1, International Atomic Energy Agency, Vienna.
Oetting, F. L. and Bixby, G. E. (1982) *J. Nucl. Mater.*, **105**, 257–61.
Oetting, F. L., Hodges, A. E., Haschke, J. M., and Flotow, H. E. (1984) *J. Chem. Thermodyn.*, **16**, 1089–102.
Ogard, A. E. (1970) in *Plutonium 1970 and Other Actinides*, vol. I, p. 78.
O'Hare, P. A. G., Flotow, H. E., and Hoekstra, H. R. (1980) *J. Chem. Thermodyn.*, **12**, 1003–8.
O'Hare, P. A. G., Malm, J. G., and Eller, P. G. (1982) *J. Chem. Thermodyn.*, **14**, 323–30.
Ohse, R. W. (1968) Institute for Transuranium Elements, Progress Report no. 5, p. 26.
Ogawa, T., Ohmichi, T., Maeda, A., Arai, Y., and Suzuki, Y. (1995) *J. Alloys Compds*, **224**, 55.

Onoe, J., Nakamatsu, H., Mukoyama, T., Sekine, R., Adachi, H., and Takeuchi, K. (1997) *Inorg. Chem.*, **36**, 1934.

Osborne, D. W., Flotow, H. E., Fried, S. M., and Malm, J. G. (1974) *J. Chem. Phys.*, **61**, 1463.

Palenzona, A. and Cirafici, S. (1975) *Thermochim. Acta*, **13**, 357–61.

Paine, R. T., McDowell, R. S., Asprey, L. B., and Jones, L. H. (1976) *J. Chem. Phys.*, **64**, 3081.

Pedley, J. B. and Marshall, E. M. (1983) *J. Phys. Chem. Ref. Data*, **12**, 967–1031.

Peng, S. and Grimvall, G. (1994) *J. Nucl. Mater.*, **210**, 115–22.

Perethrukhin, V. F., Shilov, V. P., and Pikaev, A. K. (1995) Technical Report-0817, Westinghouse Hanford Company, Richland, WA, USA.

Peterson, J. R. and Burns, J. H. (1973) *J. Inorg. Nucl. Chem.*, **35**, 1525.

Plambeck, J. A. (1976) Encyclopedia of electrochemistry of the elements, vol. X, *Fused Salt Systems* (ed. A. J. Bard), Marcel Dekker, New York.

Popov, M. M., Gal'chenko, G. L., and Senin, M. D. (1959) *Russ. J. Inorg. Chem.*, **4**, 560.

Prabhahara, R. B., Babu, R, Nagarajan, K., and Vasudeva- Rao, P. R. (1998) *J. Alloys Compds*, **271–273**, 395–8.

Prasad, R., Dash, S., Parida, S. C., Singh, Z., and Venugopal, V. (2000) *J. Nucl. Mater.*, **277**, 45–8.

Privalov, T., Schimmelpfennig, B., Wahlgren, U., and Grenthe, I. (2002) *J. Phys. Chem.*, **106**, 11277.

Rand, M. H. and Kubaschewski, O. (1963) *The Thermochemical Properties of Uranium Compounds*, Interscience, New York.

Rand, M. H. (1966) *At. Energy Rev.*, **4**, Spec. Issue no. 1, 7–51.

Rand, M. H. (1968) *Technical Panel on Uranium and Plutonium Carbides*, International Atomic Energy Agency, Vienna.

Rand, M. H. (1975) *At. Energy Rev.*, Spec. Issue no. 5, 7–85.

Robbins, D. A. and Jenkins, J. (1955) *Acta Metall.*, **3**, 598–605.

Ronchi, C. and Hiernaut, J. P. (1996) *J. Alloys Compds*, **240**, 179–85.

Ronchi, C., Capone, F., Colle, J. Y., and Hiernaut, J. P. (2000) *J. Nucl. Mater.*, **280**, 111–15.

Ronchi, C., Iosilevsji, I. L., and Yakub, E. (2002) *Equation of State of Uranium Dioxide*, Springer, Berlin, 2004.

Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, L. (1952) *Selected Values of Chemical Thermodynamic Properties*, U.S. Natl. Bur. Stand. Circ. 500, U.S. Govt. Printing Office, Washington, DC.

Roy, J. J., Grantham, L. F., Grimmett, D. L., Fusselman, S. P., Krueger, C. L., Strovick, T. S., Inoue, T., Sakamura, Y., and Takahashi, N. (1996) *J. Electrochem. Soc.*, **143**, 2487–93.

Samhoun, K. and David, F. (1976) in *Transplutonium Elements, Proc. 4th Int. Transplutonium Elements Symp.*(eds. W. Müller and R. Linder), North Holland, Amsterdam, pp. 297–319.

Santos, M., Marçalo, J., Pires de Matos, A., Gibson, J. K., and Haire, R.G. (2002a) *J. Phys. Chem. A*, **106**, 7190–4.

Santos, M., Marçalo, J., Leal, P., Pires de Matos, A., Gibson, J. K., and Haire, R. G. (2002b) *Int. J. Mass Spectrom.*, **228**, 457–65.

Schoebrechts, J.-P., Fuger, J., and Morss, L. R. (1989) *Thermochim. Acta*, **139**, 49–55.

Seaborg, G. T., Katz, J. J., and Manning, W. M. (eds.) (1949) *The Transuranium Elements: Research Papers*, Natl. Nucl. En. Ser., Div. IV, 14B, McGraw-Hill, New York.

Seleznev, A. G., Kosulin, N. S., Kosenkov, V. M., Shushakov, V. D., Stupin, V. A., Demeshkin, V. A. (1977) *Fiz. Met. Metall.*, **44**, 654–7.

Seleznev, A. G., Shushakov, V. D., and Kosulin, N. S. (1978) *Fiz. Met. Metall.*, **46**, 1109–12.

Serizawa, H., Arai, Y., and Nakajima, K. (2001) *J. Chem. Thermodyn.*, **33**, 615–28.

Serp, J., Konings, R. J. M., Malmbeck, R., Rebizant, J., Scheppler, C., and Glatz, J.-P. (2004) *J. Electroanal. Chem.*, **561**, 143–8.

Shannon, R. D. (1976) *Acta Crystallogr. A*, **32**, 751–67.

Shock, E. L., Sassani, D. C., Willis, M., and Svergensky, D. A. (1997) *Geochim. Cosmochim. Acta*, **61**, 907–50.

Silva, R. J., McDowell, W. J., Keller, Jr, and O. L. Tarrant, J. R. (1974) *Inorg. Chem.*, **13**, 2233–8.

Silva, R. J. (1982) Lawrence Berkeley Laboratory Report LBL-15055, 57 pp.

Silva, R. J., Bidoglio, G. R., Rand, M. H., Robouch, P. B., Wanner, H., and Puigdomenech, I. (1995) *Chemical Thermodynamics of Americium*, Elsevier, Amsterdam.

Simakin, G. A., Baranov, A. A., Kosyakov, V. N., Timofeev, G. A., Erin, E. A., and Lebedev, I. A. (1977) *Sov. Radiochem.*, **19**, 307–9.

Smith, P. K. and Peterson, D. E. (1970) *J. Chem. Phys.*, **52**, 4963–70.

Souter, P. F. and Andrews, L. (1997) *J. Mol. Struct.*, **412**, 161–5.

Tagawa, H. (1974) *J. Nucl. Mater.*, **51**, 78–89.

Takahashi, K., Fujino, T., and Morss, L. R. (1993) *J. Solid State Chem.*, **105**, 234–42.

Tasker, I., O'Hare, P. A. G., Lewis, B. M., Johnson, G. K., and Cordfiunke, E. H. P. (1988) *Can. J. Chem.*, **66**, 620–5.

Thiriet, C. and Konings, R. J. M. (2003) *J. Nucl. Mater.*, **320**, 292–8.

Turcotte, R. P., Chikalla, T. D., and Eyring, L. (1971) *J. Inorg. Nucl. Chem.*, **33**, 3749–60.

Turcotte, R. P., Chikalla, T. D., and Eyring, L. (1973) *J. Inorg. Nucl. Chem.*, **35**, 809–17.

Turcotte, R. P., Chikalla, T. D., and Haire, R. G. (1980) *J. Inorg. Nucl. Chem.*, **42**, 1729–35.

Usami, T., Kato, T., Kurata, M., Inoue, T., Sims, H. E., Beetham, S. A., and Jenkins, J. A. (2002) *J. Nucl. Mater.*, **304**, 50–5.

Venugopal, V., Kulkarni, S. G., Subbanna, C. S., and Sood, D. D. (1992) *J. Nucl. Mater.*, **186**, 259–68.

Volkov, Yu. F., Visyashcheva, G. I., Tomilin, S. V., Kapshukov, I. I., and Rykov, A. G. (1981) *Radiokhimiya*, **23**, 243–7.

Wade, W. Z. and Wolf, T. (1967) *J. Inorg. Nucl. Chem.*, **29**, 2577–82.

Wadt, W. R. and Hay, P. J. (1979) *J. Am. Chem. Soc.*, **101**, 5198–205.

Wagman, D. D., Schumm, R. H., and Parker, V. B. (1977) Report NBSIR 77–1300.

Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., and Nuttall, R. L. (1981) U.S.. Natl. Bur. Stand. Tech. Note 270–8, U.S. Govt. Printing Office, Washington, DC; (1982) *J. Phys. Chem. Ref. Data*, **11**, Suppl. 2.

Ward, J. W., Kleinschmidt, P. D., and Peterson, D. E. (1986) in *Handbook on the Physics and Chemistry of the Actinides* (eds. A. J. Freeman and C. Keller), vol. 4, ch. 7.

Ward, J. W., Batscher, W., and Rebizant, J. (1987) *J. Less Common Metals*, **130**, 431–6.

Weigel, F., Hoffmann, G., and Ter Meer, N. (1969) *Radiochim. Acta*, **11**, 210–16.
Weigel, F., Hoffmann, G., Wishnevsky, V., and Brown, D. (1974) *J. Chem. Soc. Dalton Trans.*, 1473–7.
Weigel, F. and Kohl, R. (1985) in *Americium and Curium Chemistry and Technology* (eds. N. M. Edelstein, J. D. Navratil, and W. W. Schultz), D. Reidel, Dordrecht, The Netherlands, p. 159.
Westrum, Jr and E. F. Eyring, L. (1949) in *The Transuranium Elements* (eds. G. T. Seaborg, J. J. Katz, and W. M. Manning), Natl. Nucl. En. Ser., Div. IV, 14B, McGraw-Hill, New York, paper 6.52.
Westrum, E. F. Jr, Zainel, H. A., and Jakes, D. (1980) in *Proc. Symp. Thermodyn. Nucl. Mater. 1979*, IAEA, Vienna, vol. II, pp. 143–54.
Williams, C. W., Morss, L. R., and Choi, I.-K. (1984) in *Geochemical Behavior of Disposed Radioactive Waste* (eds. G. S. Barney, J. D. Navratil, and W. W. Schulz), Am. Chem. Soc. Symp. Ser. 246, American Chemical Society, Washington, DC, pp. 323–34.
Williams, C. W., Blaudeau, J.-P., Sullivan, J. C., Antonio, M. R., Bursten, B. E., and Soderholm, L. (2001) *J. Am. Chem. Soc.*, **123**, 4346–7.
Yamashita, T., Nitani, N., Tsuji, T., and Kato, T. (1997) *J. Nucl. Mater.*, **247**, 90–3.
Yamana, H. and Moriyama, H. (2002) Personal communication.
Yamanaka, S., Kurosaki, K., Matsuda, T., and Uno, M. (2001) *J. Nucl. Mater.*, **294**, 99–103.