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Thermochemistry of the actinides

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Abstract

The measurement of equilibria by Knudsen effusion techniques and the enthalpy of formation of the actinide atoms are briefly discussed. Thermochemical data on the sublimation of the actinide fluorides are used to calculate the enthalpies of formation and entropies of the gaseous species. Estimates are made for enthalpies and entropies of the tetrafluorides and trifluorides for those systems where data is not available. The pressure of important species in the tetrafluoride sublimation processes is calculated based on this thermochemical data.

1. Introduction

Thermochemical data for the actinide series is sparse when compared with other elements in the periodic table (see for example the tables in ref. 1). This is due to the small quantities of elements available as samples, special precautions and hazards, short half-lives, and difficulty in obtaining reliable thermochemical data from small quantities of materials. It is therefore necessary to extrapolate and estimate thermodynamic functions as a function of atomic number. This paper will examine trends in the enthalpy and entropy of gaseous and solid actinide fluorides. These quantities will be related to measured enthalpies and entropies of sublimation and to dissociation energies.

2. Thermochemical measurements

Thermochemical data are obtained from calorimetry, measurement of equilibria with the gas phase, and e.m.f. measurements [1]. This paper covers equilibria with the gas phase by measurement of the rate of evaporation from an effusion cell. Free energy changes for chemical reactions are related to measured rates of evaporation or pressure. The free energy change ΔG for a given process at a temperature T is related to the enthalpy ΔH change and entropy ΔS change and to the equilibrium constant K for a reaction by the equations:

$$\Delta G = \Delta H - T\Delta S = -RT \ln K \quad (1)$$

where R is the gas constant. In reactions in which a solid is in equilibrium with a single gas phase species, the equilibrium constant reduces to P, the pressure of the species. The reaction becomes 1 mole of solid going to 1 mole of gaseous atoms or molecules.

Measuring the pressure of an atom, A, in the simple sublimation reaction

$$\mathrm{A(s, l) = A(g)} \quad (2)$$

gives the free energy of formation of A(g). Similarly, measuring the pressure of molecule AX_n in the reaction

$$\mathrm{AX}_n\mathrm{(s, l)} = \mathrm{AX}_n\mathrm{(g)} \quad (3)$$

gives the free energy of sublimation of AX_n(s). These data are combined with the dissociation energy, D_0, of AX_n(g), the free energy of formation of the atoms A(g) and X(g), and the free energy of formation of AX_n(s) in a thermochemical cycle. The quantity D_0 refers to the enthalpy change at 0 K for the reaction

$$\mathrm{AX}_n\mathrm{(g)} = \mathrm{A(g)} + n\mathrm{X(g)} \quad (4)$$

In the Knudsen effusion technique [1], the pressure is proportional to the rate of loss of material from the cell. This rate is determined by weighing the cell, condensing the beam on a target, or detecting the effusing beam with a mass spectrometer.

The relation between the pressure P of a gas phase species and the ion current I^+ it produces in a mass spectrometer is

$$P = CI^+T \quad (5)$$

where C is an instrumental constant depending on the geometry of the system, the ionization cross-section, the detector efficiency, the electron beam energy and the appearance potential of the detected species $\mathrm{AnX}_m{}^+$. With the use of an electron impact ion source on the mass spectrometer, one can also obtain thermochemical data by measuring ionization and fragment ion appearance potentials.

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3. Actinide elements

Measurement of the enthalpy of sublimation of the actinide elements gives the cohesive energy of the metals (the energy difference between the gaseous atoms and the metal). Figure 1 shows the enthalpy of formation of the gaseous atoms [2,3]. The enthalpy of formation of the actinide atoms is equal to the enthalpy of sublimation. All actinide metals whose enthalpy of sublimation has been measured sublime predominantly to the atomic species.

Only actinium and the elements beyond mendelevium have not been measured. The cohesive energy of the early actinides has a contribution from f electron bonding. After Pu in the periodic table this effect is not present, and the series behaves like the lanthanides until Es is reached. At Es the metal becomes divalent like Ba. Since not all gas phase atoms are in the same valence state as they are in the metal, a correction equal to the excitation energy to the trivalent state is added to the enthalpy of sublimation [4]. The constancy of this function is apparent in the part of the series running from Am to Cf, the region in which the metals should be trivalent. The entropies of the actinide atoms have been calculated from the electronic energy levels of the atoms [2].

4. Actinide fluorides

The actinide fluorides have the largest enthalpies of formation of the actinide halides and they can have valencies up to 6 for U, Np and Pu [5,6]. Sublimation data are available for UF_6 [5], NpF_6 [5], PuF_6 [5], ThF_4 [7], UF_4 [8], NpF_4 [9], PuF_4 [10], PuF_3 [11], AmF_3 [12], and CfF_3 [13]. The enthalpies and entropies of sublimation for the reaction

$$AnF_n(s) = AnF_n(g) \qquad (6)$$

are given in Table 1, where $n = 3$ and 4.

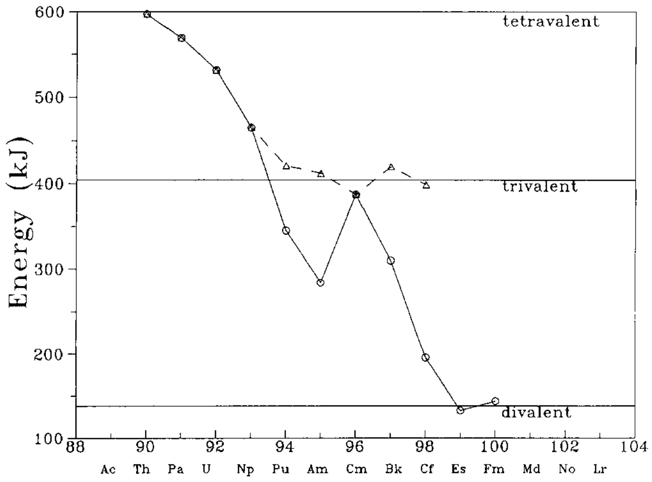

Fig. 1. Enthalpy of sublimation of the elements. The solid line with circles is the measured enthalpy of sublimation. The dashed line with triangles is the energy required to sublime one mole of atoms plus the energy required to excite an atom from a divalent to a trivalent electronic state.

The enthalpies of formation of solid actinide fluorides are shown in Table 2. Most of the enthalpies of formation of the tetrafluorides and trifluorides have been estimated [5,6]. Tetrafluorides formed from einsteinium and higher atomic numbered elements are unstable relative to the trifluorides. Thorium and protactinium are not known to form trifluorides.

The entropies of the solid fluorides are shown in Table 3. The entropies of the tetrafluorides and trifluorides which have not been measured are estimated assuming that the spin contribution is the only difference in the entropy in going to heavier elements.

The enthalpies of formation of the gaseous species (shown in Table 4) can be calculated from the enthalpy of formation of the solid and the enthalpy of sublimation. The enthalpy of sublimation has been linearly extrapolated for the trifluorides to the heavier actinides so that the enthalpy of formation of these species can be calculated.

For those species such as $ThF_3(g)$ which cannot be generated directly by sublimation of a solid, the enthalpy of formation can be calculated from the thermochemical cycle

$$AnF_n(g) \longrightarrow An(g) + nF(g) \longrightarrow An(s) + (n/2)F_2(g) \longrightarrow AnF_n(g) \qquad (7)$$

The data needed to complete the cycle besides the enthalpy of formation of $AnF_n(g)$ include the enthalpy of formation of the atoms and the dissociation (atomization) energy. The relationship between the disso-

TABLE 1. Enthalpies and entropies of sublimation of actinide tetrafluorides and trifluorides at 298 K

AnF_n	$\Delta_{sub}H^0$ (298) (kJ mole^{-1})	$\Delta_{sub}S^0$ (298) (J K^{-1} mole^{-1})	Ref.
ThF_4	338.4 ± 4.0	203.1 ± 4.0	7
PaF_4	(326.0 ± 20)	(215.0 ± 13)	est.
UF_4	318.8 ± 2.1	218.2 ± 6.3	8
NpF_4	288.1 ± 3.6	199.1 ± 11.0	9
PuF_4	286.0 ± 2.1	192.9 ± 2.4	10
AmF_4	(269.0 ± 20)	(211.0 ± 13)	est.
PuF_3	429.5 ± 4.7	209.7 ± 3.3	11
AmF_3	427.7 ± 2.2	213.3 ± 1.7	12
CmF_3	(426.0 ± 20)	(214.0 ± 21)	est.
BkF_3	(424.0 ± 20)	(214.0 ± 21)	est.
CfF_3	430.9 ± 5.4	212.9 ± 4.3	13
EsF_3	(420.0 ± 20)	(215.0 ± 21)	est.

TABLE 2. Enthalpies of formation, $\Delta_f H^0$ (AnF_n, s, 298), of solid actinide fluorides. Values in kJ mole^{-1}

An	AnF_6	Ref.	AnF_4	Ref.	AnF_3	Ref.
Ac	*		*		(−1659.0±45)	5
Th	*		−2098.0±8	5,6	*	
Pa	*		(−1946.0±17)	5,6	*	
U	−2197.0+2.0	5,6	−1914.0±4	5,6	−1502.0±4	5,6
Np	–		(−1874.0±13)	5,6	(−1530.0±5)	5,6
Pu	−2025.0+42.0	14	(−1846.0±21)	5,6	−1586.0±3	5,6
Am	–		(−1720.0±29)	5,6	(−1588.0±13)	5,6
Cm	*		(−1689.0)	6	(−1599.0±18)	6
Bk	*		(−1793.0)	6	(−1581.0)	6
Cf	*		(−1623.0)	6	(−1553.0±35)	6
Es	*		(−1521.0)	6	(−1575.0±40)	6

( ) = estimate, * = not stable, – = data not available.

TABLE 3. Entropies, S^0(AnF_n, s, 298), of solid actinide fluorides. Values in J K^{-1} mole^{-1}

An	AnF_6	Ref.	AnF_4	Ref.	AnF_3	Ref.
Ac	*		*		(112.0±6)	
Th	*		142.0±0.2	5,6	*	
Pa	–		(146.9±4)	5,6	*	
U	227.6±13	5,6	151.7±0.2	5,6	123.4±0.4	5,6
Np	229.1±0.5	6	(153.0±4)	5,6	125.0±4	5,6
Pu	222.0±21	6	147.2±0.4	5,6	126.1±0.4	5,6
Am	–		(148.5±4)	5,6	(128.0±4)	5,6
Cm	*		(150.0±6)		(129.0±6)	
Bk	*		(151.0±6)		(128.0±6)	
Cf	*		(150.0±6)		(126.0±6)	
Es	*		(149.0±6)		(125.0±6)	

( ) = estimated value, * = not stable, – = data not available.

TABLE 4. Enthalpies of formation, $\Delta_f H^0$(AnF_n, g, 298), of gaseous actinide fluorides. Values in kJ mole^{-1}

An	AnF_4	Ref.	AnF_3	Ref.	AnF_2	Ref.
Ac	*		–		–	
Th	−1759.0	7	−1171.5±12	7	−597.9±10	7
Pa	(−1620.0±26)		–		–	
U	−1602.9±4.6	15	−1084.9±12.6	15	−540.6±10.5	15
Np	−1586.0±17	9	(−1099.0±21)		–	
Pu	−1560.0±21	10	−1156.0±6	11	−615.8±21	16
Am	(−1451.0±35)		−1160.0±13	12	–	
Cm	–		(−1173.0±27)		–	
Bk	–		(−1157.0±35)		–	
Cf	–		−1102.0±35	13	–	
Es	–		(−1155.0±45)		–	

( ) = estimated values, * = not stable, – = data not available.

ciation energy and the enthalpy of formation of AnF_n(g) is

$$\Delta_f H(AnF_n, 298) = D_0 + \Delta(H^0(298\ K) - H^0(0\ K)) + \Delta_f H^0(An, g) + (n/2)\Delta_f H^0(X, g) \quad (8)$$

Bond dissociation energies measured from gas phase equilibria [7,14,16] were used to calculate the dissociation energies of the trifluorides and difluorides where known. If the enthalpy of formation is known from sublimation reactions, the dissociation energy can be calculated if the enthalpy of formation of the atoms is known.

The entropies of the gaseous species are given in Table 5. For those species for which no information is available in the literature, the entropy has been calculated by assuming that the structure and vibrational

TABLE 5. Entropy, $S^0(\mathrm{AnF}_n$, g, 298), of gaseous actinide fluorides. Values in J K^{-1} mole^{-1}

An	AnF_4	Ref.	AnF_3	Ref.	AnF_2	Ref.
Ac	*		(324.9 ± 20)		–	
Th	345.1 ± 4.0	7	335.4 ± 12	7	297.9 ± 10	7
Pa	(362.0 ± 15)		(334.0 ± 20)		–	
U	364.4 ± 4.2	15	355.3 ± 20	15	328.0 ± 12	15
Np	351.8 ± 12	9	(339.0 ± 20)		–	
Pu	340.2 ± 2.4	10	335.8 ± 3.3	11	297.0	16
Am	(360.0 ± 15)		340.9 ± 4.3	12	–	
Cm	–		(343.0 ± 20)		–	
Bk	–		(342.0 ± 20)		–	
Cf	–		339.4 ± 5.9	13	–	
Es	–		(340.0 ± 20)		–	

( ) = estimated value, * = not stable, – = data not available.

frequencies are the same as those given for UF_4 or UF_3 [17]. The atomic weights of the actinide atoms are Pa = 231.0, Np = 237.0, Cm = 248.1, Bk = 249.1 and Es = 243.1. These weights are for isotopes most likely to be used in experiments. The ground state degeneracies were assumed to be PaF_4: 2; AmF_4: 6; AcF_3: 1; PaF_3: 3; NpF_3: 5; CmF_3: 8; BkF_3: 7; and EsF_3: 5. No excited state electronic contributions were assumed. All the tetrafluoride molecules, with the exception of $ThF_4(g)$, were assumed to have C_{2v} symmetry. The trifluorides were assumed to have C_{3v} symmetry. The estimated error ranges from ± 15 to ± 20 J K^{-1} mole^{-1}.

Based upon the data given here and assuming that the free energy of formation of the species can be approximated by the relation

$$\Delta G^0(T) = \Delta H^0(298\ \mathrm{K}) - T\Delta S^0(298\ \mathrm{K}) \qquad (9)$$

the vapor species present during sublimation or evaporation can be calculated. The sublimation mechanism for the tetrafluorides is believed to occur in the temperature range 298–1000 K by the following processes:

$$\mathrm{AnF_4(s) = AnF_4(g)} \qquad (10)$$

$$\mathrm{AnF_4(s) = AnF_3(s) + F(g)} \qquad (11)$$

The first process applies to Th, Pa, U, Np and Pu and the second process applies to Cm, Bk, Cf and Es, with Am being an intermediate case.

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