

## Appendix E

# Spectroscopic constants and statistical mechanics calculations for gaseous species

In most cases, the thermal functions for gaseous species have been calculated by well-known statistical-mechanical relations (see for example Chapter 27 of [1961LEW/RAN]).

The parameters defining the vibrational and rotational energy levels of the molecule in terms of the rotational ( $J$ ) and vibrational ( $\nu$ ) quantum numbers, and thus many of its thermodynamic properties, are:

- for diatomic molecules (non-rigid rotator, anharmonic oscillator approximation):  $\omega$  (vibrational frequency in wavenumber units),  $x$  (anharmonicity constant),  $B$  (rotational constant for equilibrium position),  $D$  (centrifugal distortion constant),  $\alpha$  (rotational constant correction for excited vibrational states), and  $\sigma$  (symmetry number), where the energy levels with quantum numbers  $\nu$  and  $J$  are given by:

$$E_{(\nu,J)} / hc = \omega (\nu + 1/2) - \omega x (\nu + 1/2)^2 + B J(J+1) - D J^2 (J+1)^2 - \alpha (\nu + 1/2) J (J+1) \quad (\text{E.1})$$

- for linear polyatomic molecules, the parameters are the same as those for diatomic molecules, except that the contributions for anharmonicity are usually neglected.
- for non-linear polyatomic molecules (rigid rotator, harmonic oscillator approximation):  $I_x I_y I_z$ , the product of the principal moments of inertia (readily calculated from the geometrical structure of the molecule),  $\nu(i)$ , the vibration frequencies and  $\sigma$ , the symmetry number. While the vibrational energy levels for polyatomic molecules are given approximately by the first term of Equation (E.1) for each of the normal vibrations, the rotational energy levels cannot be expressed as a simple general formula. However, the required rotational partition function can be expressed with sufficient accuracy simply in terms of the product of the principal

moments of inertia. As for linear polyatomic molecules, anharmonic contributions are usually neglected.

In each case, the symmetry number  $\sigma$ , the number of indistinguishable positions into which the molecule can be turned by simple rotations, is required to calculate the correct entropy.

The relations for calculating the thermal functions from the partition function defined by the energy levels are well-known – again, see Chapter 27 of [1961LEW/RAN], for a simple description. In each case, the relevant translational and electronic contributions (calculated from the molar mass and the electronic energy levels and degeneracies) must be added. Except where accurate spectroscopic data exist, the geometry and parameters of the excited states are assumed to be the same as those for the ground state.

Table E-1 gives the molecular parameters of all the gaseous thorium species for which data are selected. Part A gives the selected parameters of the ground states of diatomic molecules, where  $r$  is the interatomic distance, and the remaining symbols are described above; higher electronic levels were included only for ThO(g) and ThS(g). The parameters for the excited states of ThO(g) are given in detail in Table VII-1; the energy levels assumed for ThS(g) are included below.

Table E-1: Molecular parameters of gaseous thorium species

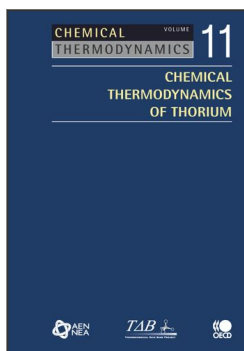
Part A: diatomic species.

	$r$ (Å)	$\omega$ (cm <sup>-1</sup> )	$\omega x$ (cm <sup>-1</sup> )	$B$ (cm <sup>-1</sup> )	$10^3 \alpha$ (cm <sup>-1</sup> )	$10^7 D$ (cm <sup>-1</sup> )	Ground-state degeneracy
Th <sub>2</sub>	3.3	92.2	0	0.01334	0	0	2
ThO	1.8403	895.77	2.39	0.332644	1.302	1.833	1
ThH	1.985	1485.2	30	4.2636	150	2000	2
ThF	2.05	489	4.0	0.2284	2.0386	1.9931	4
ThCl	2.48	292	2.0	0.089124	0.60992	0.33206	4
ThBr	2.65	194	2.0	0.040388	0.30458	0.070029	4
ThI	2.85	151	1	0.025299	0.13447	0.02841	4
ThS	2.34	480	2.39	0.1093	0	0	1
ThN	1.93	775	3.0	0.3426	0	0	2
ThP	2.67	360	0.0	0.08654	0	0	4
Additional electronic levels (cm <sup>-1</sup> ) (degeneracy)							
ThO(g)	see Table VII-1						
ThS(g)	4200(2)	4700(2)	5200(2)				

(Continued on next page)

Table E-1: (continued)  
Part B: polyatomic species.

Species	Point group (Symmetry number)	Interatomic distance (Å)	Angle (deg)	Vibration frequencies (multiplicities) (cm <sup>-1</sup> )	Product of moments of inertia (g <sup>3</sup> ·cm <sup>-6</sup> )
ThO <sub>2</sub>	C <sub>2v</sub> (2)	1.82	122.5	787(1) 220(1) 735(1)	8.28·10 <sup>-115</sup>
ThF <sub>2</sub>	C <sub>2v</sub> (2)	2.10	130	483(1) 130(1) 447(1)	2.65·10 <sup>-114</sup>
ThF <sub>3</sub>	C <sub>3v</sub> (3)	2.10	110	484(2) 156(2) 480(1) 140(1)	1.84·10 <sup>-113</sup>
ThF <sub>4</sub>	T <sub>d</sub> (12)	2.14	109.5	581.6(1) 109.3(2) 520.0(3) 116.0(3)	5.72·10 <sup>-113</sup>
ThOF	C <sub>2v</sub> (2)	Th-O 1.80 Th-F 2.10	110	750(1) 500(1) 150(1)	1.98·10 <sup>-114</sup>
ThCl <sub>2</sub>	C <sub>2v</sub> (2)	2.53	130	308(1) 84(1) 315(1)	4.61·10 <sup>-113</sup>
ThCl <sub>3</sub>	C <sub>3v</sub> (3)	2.53	110	320(1) 100(1) 333(2) 105(2)	3.49·10 <sup>-112</sup>
ThCl <sub>4</sub>	T <sub>d</sub> (12)	2.567	109.5	340.3(1) 62.0(1) 335.0(3) 61.8(3)	1.11·10 <sup>-111</sup>
ThBr <sub>2</sub>	C <sub>2v</sub> (2)	2.70	130	196(1) 60(1) 232(1)	5.83·10 <sup>-112</sup>
ThBr <sub>3</sub>	C <sub>3v</sub> (3)	2.70	110	200(1) 68(1) 223(2) 66(2)	5.45·10 <sup>-111</sup>
ThBr <sub>4</sub>	T <sub>d</sub> (12)	2.73	109.5	297.8(1) 40.4(2) 230 (3) 44.6(3)	1.83·10 <sup>-110</sup>
ThI <sub>2</sub>	C <sub>2v</sub> (2)	2.90	130	140(1) 45(1) 176(1)	2.83·10 <sup>-111</sup>
ThI <sub>3</sub>	C <sub>3v</sub> (3)	2.90	110	144(1) 53(1) 170(2) 48(2)	3.19·10 <sup>-110</sup>
ThI <sub>4</sub>	T <sub>d</sub> (12)	2.91	109.5	147.6(1) 29.0(2) 179.6(3) 33.9(3)	1.08·10 <sup>-109</sup>
ThC <sub>2</sub>	C <sub>∞</sub> (2)		180	see Table VII-1	$I_x = 2.44 \cdot 10^{-38} \text{ g} \cdot \text{cm}^{-2}$
ThC <sub>4</sub>	C <sub>∞</sub> (2)		180	761(1) 1836(1) 734(1) 1771(1) 101(2) 494(2) 437(2)	$I_x = 5.35 \cdot 10^{-38} \text{ g} \cdot \text{cm}^{-2}$
Electronic levels (cm <sup>-1</sup> ) (degeneracy)					
Th <sub>2</sub>	0(2)				
ThO <sub>2</sub>	0(1) 20000(2) 21000(2) 22000(2) 23000(2) 26000(2) 28000(2)				
ThF <sub>2</sub>	0(1)				
ThF <sub>3</sub>	0(6)				
ThF <sub>4</sub>	0(1)				
ThCl <sub>2</sub>	0(1)				
ThCl <sub>3</sub>	0(6)				
ThCl <sub>4</sub>	0(1)				
ThBr <sub>2</sub>	0(1)				
ThBr <sub>3</sub>	0(6)				
ThBr <sub>4</sub>	0(1)				
ThI <sub>2</sub>	0(1)				
ThI <sub>3</sub>	0(6)				
ThI <sub>4</sub>	0(1)				
ThC <sub>2</sub>	0(1) 5321(2) 106256(1) 11156(2) 14520(2) 15975(2) 16354(1) 18038(2) 18337.6(1) 19586(2)				
ThC <sub>4</sub>	see Table VII-1				



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