

# **Standard Thermodynamic Functions of Gaseous Polyatomic Ions at 100–1000 K**

Cite as: Journal of Physical and Chemical Reference Data **16**, 61 (1987); <https://doi.org/10.1063/1.555792>  
Submitted: 09 April 1986 . Published Online: 15 October 2009

Aharon Loewenschuss, and Yitzhak Marcus



[View Online](#)



[Export Citation](#)

## **ARTICLES YOU MAY BE INTERESTED IN**

**Standard Thermodynamic Functions of Some Isolated Ions at 100–1000 K**  
Journal of Physical and Chemical Reference Data **25**, 1495 (1996); <https://doi.org/10.1063/1.555990>

**JANAF thermochemical tables, 1978 supplement**

Journal of Physical and Chemical Reference Data **7**, 793 (1978); <https://doi.org/10.1063/1.555580>

**Thermochemical Data on Gas Phase Compounds of Sulfur, Fluorine, Oxygen, and Hydrogen  
Related to Pyrolysis and Oxidation of Sulfur Hexafluoride**

Journal of Physical and Chemical Reference Data **16**, 1 (1987); <https://doi.org/10.1063/1.555791>

Where in the world is AIP Publishing?  
*Find out where we are exhibiting next*

**AIP Publishing**

# Standard Thermodynamic Functions of Gaseous Polyatomic Ions at 100–1000 K

Aharon Loewenschuss and Yitzhak Marcus

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, 91904 Jerusalem, Israel

Received April 9, 1986; revised manuscript received July 15, 1986

The standard thermodynamic functions—heat capacity at constant pressure  $C_p^\circ$ , its ratio to that at constant volume, the entropy  $S^\circ$ , the enthalpy minus that at absolute zero ( $H^\circ - H_0^\circ$ ), and the Gibbs energy function  $(G^\circ - H_0^\circ)/T$  were calculated for 131 gaseous ions in the temperature interval 100–1000 K, and are presented in tables. The input data included structural information (bond lengths and angles), vibrational spectroscopic information (vibrational frequencies and degeneracies), and electronic level occupation and degeneracies for ions having unpaired electrons. These were taken mainly from a recent review by the authors, and supplemented by further data from the literature, updated to the end of 1985.

Key words: enthalpy; entropy; Gibbs energy; heat capacity; polyatomic ions; thermodynamic functions (ideal gas).

## Contents

1. Introduction .....	63	12. Dimercury (I), $\text{Hg}_2^{2+}$ .....	67
2. The Calculation .....	63		
3. Tables of Thermodynamic Functions .....	65		
4. Specific Comments .....	87		
5. Acknowledgments .....	89		
6. References .....	89		

## List of Tables<sup>a)</sup>

Diatomic Ions			
1. Hydroxide, $\text{OH}^-$ .....	65	12. Dimercury (I), $\text{Hg}_2^{2+}$ .....	67
2. Hydrosulfide, $\text{HS}^-$ .....	65		
3. Hydroselenide, $\text{HSe}^-$ .....	65		
4.* Superoxide, $\text{O}_2^-$ .....	65		
5. Peroxide, $\text{O}_2^{2-}$ .....	65		
6. Hypochlorite, $\text{ClO}^-$ .....	66		
7. Hypobromite, $\text{BrO}_2^-$ .....	66		
8. Nitrosonium, $\text{NO}^+$ .....	66		
9.* Vanadyl (IV), $\text{VO}^{2+}$ .....	66		
9a. Antimonyl (III), $\text{SbO}^+$ .....	66		
10. Cyanide, $\text{CN}^-$ .....	66		
11. Disulfide, $\text{S}_2^{2-}$ .....	67		
Triatomic Ions			
13. Azide, $\text{N}_3^-$ .....	67	13. Azide, $\text{N}_3^-$ .....	67
14. Trisulfide, $\text{S}_3^{2-}$ .....	67	14. Trisulfide, $\text{S}_3^{2-}$ .....	67
15. Tribromide, $\text{Br}_3^-$ .....	67	15. Tribromide, $\text{Br}_3^-$ .....	67
16. Triiodide, $\text{I}_3^-$ .....	67	16. Triiodide, $\text{I}_3^-$ .....	67
17. Hydrogendifluoride, $\text{HF}_2^-$ .....	68	17. Hydrogendifluoride, $\text{HF}_2^-$ .....	68
18. Hydroperoxide, $\text{HO}_2^-$ .....	68	18. Hydroperoxide, $\text{HO}_2^-$ .....	68
19.* Metaborate, $\text{BO}_2^-$ .....	68	19.* Metaborate, $\text{BO}_2^-$ .....	68
20. Metaaluminate, $\text{AlO}_2^-$ .....	68	20. Metaaluminate, $\text{AlO}_2^-$ .....	68
21. Nitronium, $\text{NO}_2^+$ .....	68	21. Nitronium, $\text{NO}_2^+$ .....	68
22. Nitrite, $\text{NO}_2^-$ .....	68	22. Nitrite, $\text{NO}_2^-$ .....	68
23. Chlorite, $\text{ClO}_2^-$ .....	69	23. Chlorite, $\text{ClO}_2^-$ .....	69
23a. Bromite, $\text{BrO}_2^-$ .....	69	23a. Bromite, $\text{BrO}_2^-$ .....	69
23b. Metaarsenite, $\text{AsO}_2^-$ .....	69	23b. Metaarsenite, $\text{AsO}_2^-$ .....	69
24. Dioxovanadium(V), $\text{VO}_2^+$ .....	69	24. Dioxovanadium(V), $\text{VO}_2^+$ .....	69
25. Dioxouranium(VI), $\text{UO}_2^{2+}$ .....	69	25. Dioxouranium(VI), $\text{UO}_2^{2+}$ .....	69
25a.* Dioxoneptunium(VI), $\text{NpO}_2^{2+}$ .....	69	25a.* Dioxoneptunium(VI), $\text{NpO}_2^{2+}$ .....	69
25b.* Dioxoplutonium(VI), $\text{PuO}_2^{2+}$ .....	70	25b.* Dioxoplutonium(VI), $\text{PuO}_2^{2+}$ .....	70
25c.* Dioxoamericium(VI), $\text{AmO}_2^{2+}$ .....	70	25c.* Dioxoamericium(VI), $\text{AmO}_2^{2+}$ .....	70
26.* Dioxouranium(V), $\text{UO}_2^+$ .....	70	26.* Dioxouranium(V), $\text{UO}_2^+$ .....	70
26a.* Dioxoneptunium(V), $\text{NpO}_2^+$ .....	70	26a.* Dioxoneptunium(V), $\text{NpO}_2^+$ .....	70
26b.* Dioxoplutonium(V), $\text{PuO}_2^+$ .....	70	26b.* Dioxoplutonium(V), $\text{PuO}_2^+$ .....	70
26c.* Dioxoamericium(V), $\text{AmO}_2^+$ .....	70	26c.* Dioxoamericium(V), $\text{AmO}_2^+$ .....	70
27. Cyanate, $\text{NCO}^-$ .....	71	27. Cyanate, $\text{NCO}^-$ .....	71
28. Thiocyanate, $\text{SCN}^-$ .....	71	28. Thiocyanate, $\text{SCN}^-$ .....	71
29. Dichloroargentate(I), $\text{AgCl}_2^-$ .....	71	29. Dichloroargentate(I), $\text{AgCl}_2^-$ .....	71
30. Dibromoargentate(I), $\text{AgBr}_2^-$ .....	71	30. Dibromoargentate(I), $\text{AgBr}_2^-$ .....	71
31.* Diiodoargentate, $\text{AgI}_2^-$ .....	71	31.* Diiodoargentate, $\text{AgI}_2^-$ .....	71

<sup>a)</sup> Tables for which there are comments in Sec. 4 are marked with an asterisk after their number. The tables are numbered in concordance with Ref. 4, hence in some cases numbering such as 25, 25a, 25b, etc., occurs in order to accommodate ions which have not been included in the tables of Ref. 4.

©1987 by the U. S. Secretary of Commerce on behalf of the United States. This copyright is assigned to the American Institute of Physics and the American Chemical Society.

Reprints available from ACS; see Reprints List at back of issue.



## 1. Introduction

Thermodynamic properties of polyatomic ionic species which exist, with reasonable stability, in aqueous solutions are included in the standard tabulations to a limited extent only. In the JANAF Tables,<sup>1</sup> only a small number of them are covered, whereas Barin and Knacke<sup>2</sup> limit themselves to neutral species.<sup>b</sup> On the other hand, the thermodynamic functions of such ions may be considered as quantities of interest in their own right, as well as being important in relation to chemical processes they might undergo like decomposition, association to complex ions, solvation in general, or hydration<sup>3</sup> in particular.

With the above motivation in mind, we have recently<sup>4</sup> critically reviewed the available literature on structural and spectroscopic data of over a hundred polyatomic ions and calculated from them  $S_{298}^{\circ}$ , their ideal gas standard state entropies at 298.15 K. In the present work, we extend the computation to a general tabulation of the thermodynamic functions, following the pattern of the standard compilations.<sup>1,2</sup> The molecular data chosen were given in our previous review,<sup>4</sup> along with the considerations that led to their selection when more than a single set (complete or partial) was available or to their estimation when certain data were not established experimentally. To facilitate reference to these data, the numbering of ions in this work is identical to that in Ref. 4.

In addition to the ionic species covered in the review<sup>4</sup> we have calculated in a similar manner the thermodynamic properties of the several actinyl ions  $\text{MO}_2^{n+}$  ( $n = 1$  or 2)<sup>5</sup> and of some tetrahedral M-phenyl ionic species.<sup>6</sup> In the present study we have additionally included some 15 ions not discussed by us previously. For these the data are included in the text with specific comments on the data and their selection. In the selection of ions for our compilations we were guided by the availability of sufficient structural and spectroscopic data (which includes our ability to suggest reasonable estimates for the missing quantities) and the relevance of the calculation to hydration and solvation processes. A partial tabulation of the thermodynamic functions for several of the species is given in a recent book by Krestov.<sup>7</sup> The temperature range covered in the tables, similar to that in the standard compilations,<sup>1,2</sup> is somewhat arbitrary. No association or decomposition processes that may take place within this range were taken into consideration. Actually, the availability of the thermodynamic quantities may prove relevant to the stability of these ions relative to the products in the consideration of such processes. Similarly, the calculations do not include effects of anharmonicities in the vibration, rotation-vibration interactions, and nonrigidity of the molecular rotator. In the text below the basis of the calculation is summarized and then specific comments are given for several of the entries. In these we also point out the few deviations of our evaluations from JANAF<sup>1</sup> values that go beyond the estimated errors in the calculated quantities.

## 2. The Calculation

As pointed out in the previous section, the calculations of the thermodynamic functions in this, as well as in previous<sup>1,2</sup> compilations, are based upon the ideal gas approximation and assume the separability of the translational, rotational, vibrational, and electronic degrees of freedom and therefore also the additivity of their contributions to the calculated values. In addition, the ideal models of the rigid rotator for the molecular rotation and the harmonic oscillator for the internal vibrations are assumed. These assumptions also limit the temperature range for which these calculations may be considered to be valid. The expressions below and the tabulated values are all for the standard pressure of 0.101 325 MPa. The numerical constants in the expressions below include fundamental physical constants the values of which were taken from Ref. 1 (inconsistencies with more modern values lead to deviations that are far below the estimated error in the evaluated quantities).

The translational contributions are calculated by the following simple expressions. For the heat capacity at constant pressure:

$$C_{p,\text{trans}} = (5/2)R \text{ J/(K mol)}, \quad (1)$$

for the entropy:

$$S_{\text{trans}} = R(1.5 \ln M + 2.5 \ln T) - 9.686 \text{ J/(K mol)}, \quad (2)$$

for the enthalpy:

$$(H - H_0)_{\text{trans}} = (5/2)RT \text{ kJ/mol}, \quad (3)$$

for the Gibbs energy function:

$$- [G - H_0]/T]_{\text{trans}} = R [1.5 \ln M + 2.5 \ln T] - 30.472 \text{ J/(K mol)}, \quad (4)$$

where  $R = 8.3144 \text{ J/(K mol)}$  is the ideal gas constant,  $M$  is the molecular mass in u, and  $T$  is the temperature in K. The numerical constants in the expressions are derived from the values of universal constants and the imposition of the standard pressure condition.

For the rotational contributions (nonlinear ions) the following expressions are applied. For the heat capacity at constant pressure:

$$C_{p,\text{rot}} = (3/2)R \text{ J/(K mol)}, \quad (5)$$

for the entropy:

$$S_{\text{rot}} = R [0.5 \ln D + 1.5 \ln T - \ln \sigma] - 34.904 \text{ J/(K mol)}, \quad (6)$$

for the enthalpy:

$$(H - H_0)_{\text{rot}} = (3/2)RT \text{ kJ/mol}, \quad (7)$$

for the Gibbs energy function:

$$- [(G - H_0)/T]_{\text{rot}} = R [0.5 \ln D + 1.5 \ln T - \ln \sigma] + 22.432 \text{ J/(K mol)}. \quad (8)$$

Here  $D$  is the determinant of the moments of inertia,

$$D = \begin{vmatrix} I_x & -I_{xy} & -I_{xz} \\ -I_{yx} & I_y & -I_{yz} \\ -I_{zx} & -I_{zy} & I_z \end{vmatrix} (\text{u nm}^2)^3, \quad (9)$$

<sup>b</sup> One of the referees called our attention to the recent Russian IVTAN compilation of thermodynamic functions, which is presently unavailable to us. According to this information the only ion not also covered by JANAF (Ref. 1) is  $\text{HO}_2^-$ .

with components  $I_x = \sum_i m_i (y_i^2 + z_i^2)$ ,  $I_{xy} = \sum_i m_i x_i y_i$ , and their respective analogs, with  $m_i$  the atomic masses in  $u$  and  $x_i, y_i, z_i$  their Cartesian coordinates in nm as measured from the molecular center of mass. The symmetry number  $\sigma$  denotes the number of equivalent molecular positions the ion passes through during one full rigid rotation.

For linear ions which have only two (as opposed to three) rotational degrees of freedom and a single moment of inertia, Eqs. (5)–(9) have to be replaced by

$$C_p \text{rot(lin)} = R \text{ J/(K mol)}, \quad (5a)$$

$$S_{\text{rot(lin)}} = R(1 - \ln y - \ln \sigma) \text{ J/(K mol)} \quad (6a)$$

$$[H - H_0]_{\text{rot(lin)}} = RT(1 - y/3) \text{ kJ/mol}, \quad (7a)$$

for the Gibbs energy function:

$$\begin{aligned} & -[(G - H_0)/T]_{\text{rot(lin)}} \\ & = R(-\ln y - \ln \sigma + y/3) \text{ J/(K mol)}, \end{aligned} \quad (8a)$$

$y$  is related to the moment of inertia  $I$  by:

$$y = 0.24254/(IT) \text{ (u nm}^2 \text{ K})^{-1}, \quad (9a)$$

with  $I = \sum_i m_i x_i^2$  and, as before,  $m_i$  are the atomic masses in  $u$  and  $x_i$  their Cartesian coordinates in nm as measured from the molecular center of mass.

The vibrational contribution to the thermodynamic functions is the sum of the contributions of the  $(3n - 6)$  vibrational degrees of freedom for nonlinear ions or the  $(3n - 5)$  vibrational degrees of freedom for linear ions. The pertinent expressions below are written for the contribution of each normal mode and, therefore, the degeneracy factor  $d(i)$  is included. For the heat capacity at constant pressure:

$$C_p(i)_{\text{vib}} = d(i)R \frac{u(i)^2 e^{u(i)}}{[e^{u(i)} - 1]^2} \text{ J/(K mol)}, \quad (10)$$

for the entropy:

$$S(i)_{\text{vib}} = d(i)R \left\{ \frac{u(i)}{e^{u(i)} - 1} - \ln[1 - e^{-u(i)}] \right\} \text{ J/(K mol)}, \quad (11)$$

for the enthalpy:

$$[H(i) - H_0(i)]_{\text{vib}} = d(i)RT \frac{u(i)e^{-u(i)}}{1 - e^{-u(i)}} \text{ kJ/mol}, \quad (12)$$

for the Gibbs energy function:

$$\begin{aligned} & -\{[G(i) - H_0(i)]/T\}_{\text{vib}} \\ & = -d(i)R\{\ln[1 - e^{-u(i)}]\} \text{ J/(K mol)}, \end{aligned} \quad (13)$$

$u(i)$  is related to the frequency  $v(i)$  of the vibrational normal mode  $(i)$  by:

$$u(i) = 1.4388v(i)/T \text{ cm}^{-1}/\text{K}. \quad (14)$$

In the case of three metal ammine complex ions, we assumed free rotations of the ammine groups against the rest of the molecule. Such an assumption has the effect of changing the value of the symmetry number  $\sigma$  to that appropriate when the rotating groups are considered as point masses. Additionally, for the torsional modes the vibrational contributions of Eqs. (10)–(14) are replaced by the following. For the heat capacity at constant pressure:

$$C_p \text{free rot} = 0.5n(i)R \text{ J/(K mol)}, \quad (15)$$

for the entropy:

$$\begin{aligned} S_{\text{free rot}} & = 0.5n(i)R(\ln I_r - \ln \sigma' + \ln T) \\ & + 14.803 \text{ J/(K mol)}, \end{aligned} \quad (16)$$

for the enthalpy:

$$(H - H_0)_{\text{free rot}} = 0.5n(i)RT \text{ kJ/mol}, \quad (17)$$

for the Gibbs energy function:

$$\begin{aligned} & -[(G - H_0)/T]_{\text{free rot}} = 0.5n(i)R(\ln I_r - \ln \sigma' + \ln T) \\ & + 10.646 \text{ J/(K mol)}, \end{aligned} \quad (18)$$

$n(i)$  is the number of freely rotating ammine groups, and  $I_r$  is the reduced moment of inertia:

$$I_r = I_A I_B / (I_A + I_B) \text{ u nm}^2, \quad (19)$$

with  $I_A$  and  $I_B$  being the moments of inertia of the parts A and B of the molecule rotating against each other.  $\sigma'$  is the symmetry number denoting the number of identical molecular orientations the ion attains during an internal rotation of part A against part B. In the other cases, where the complement of vibrational modes includes torsional motions, we found that the calculated<sup>8</sup> potential barrier for hindered rotation is high enough, relative to the temperature range considered here, for the regular expressions for the vibrational contributions of Eqs. (10)–(14) to be applicable.

For ions with unpaired electrons, we also included the contributions of the electronic energy levels to the computed thermodynamic functions. As there is no regularity in the energy and degeneracy of the electronic levels their contributions to the partition function have to be summed individually. Fortunately, only the lowest levels have to be considered, as the contribution of energy levels above  $5000 \text{ cm}^{-1}$  is negligible even at 1000 K. This evaluation of the electronic contributions improves slightly the simpler calculation employed for this term in our previous publication on the entropies at 298.15 K.<sup>4</sup>

The term in the partition function  $q(i)$  related to an electronic level of energy  $E(i)$  is

$$q(i) = [2j(i) + 1]e^{-u(i)}. \quad (20)$$

Here,  $u(i)$  is defined by Eq. (14) but with  $E(i)$  replacing  $v(i)$ . The preexponential term is the degeneracy as characterized by the quantum number of the total angular momentum (spin-orbit coupled)  $j(i)$ . The electronic partition function is then the sum

$$Q_{\text{el}} = \sum_i q(i). \quad (21)$$

The resulting electronic contributions to the thermodynamic functions are given by the following. For the heat capacity at constant pressure:

$$C_{p,\text{el}} = R \sum_i [u(i)^2 q(i) - u(i)q(i)/Q_{\text{el}}]/Q_{\text{el}} \text{ J/(K mol)}, \quad (22)$$

for the entropy:

$$S_{\text{el}} = R \sum_i [u(i)q(i)/Q_{\text{el}}] + R \ln Q_{\text{el}} \text{ J/(K mol)}, \quad (23)$$













































Table 119.\* Thermodynamic functions of tetrphenylphosphonium ( $C_{16}H_{13}^+$ ) $P^-$ 

T	$C_p$	$C_p/C_v$	S	H-H <sub>0</sub>	$-(\Delta H_\infty)/T$
K	J/K/mol		J/K/mol	kJ/mol	J/K/mol
100	145.48	1.061	398.8	9.18	307.0
150	194.33	1.045	466.9	17.66	349.2
200	248.45	1.035	550.1	28.70	386.5
250	307.68	1.028	591.8	42.59	421.4
273.15	335.87	1.025	620.3	50.04	437.1
298.15	366.26	1.023	651.0	58.82	453.7
300	366.50	1.023	653.3	59.89	454.9
350	427.53	1.020	714.5	79.41	487.7
400	482.69	1.018	775.3	102.19	519.8
450	533.07	1.016	835.1	127.60	551.5
500	578.52	1.015	893.7	155.41	582.8
550	619.35	1.014	950.7	185.37	613.7
600	654.01	1.013	1004.2	217.28	644.1
650	688.99	1.012	1060.1	250.91	674.1
700	718.76	1.012	1112.2	286.12	705.5
750	745.73	1.011	1162.8	322.74	732.4
800	770.23	1.011	1211.7	360.65	760.9
850	792.57	1.011	1259.1	399.73	788.8
900	812.98	1.010	1304.9	439.88	816.2
950	831.67	1.010	1349.4	481.00	843.1
1000	848.83	1.010	1392.5	523.02	884.5

Table 120.\* Thermodynamic functions of tetrphenylarsenium ( $C_{16}H_{13}^+$ ) $As^-$ 

T	$C_p$	$C_p/C_v$	S	H-H <sub>0</sub>	$-(\Delta H_\infty)/T$
K	J/K/mol		J/K/mol	kJ/mol	J/K/mol
100	148.47	1.059	394.6	9.11	303.5
150	197.43	1.044	464.0	17.75	345.6
200	251.32	1.034	528.0	28.95	383.3
250	310.29	1.028	590.4	42.97	418.5
273.15	338.36	1.025	619.1	50.48	434.3
298.15	368.62	1.023	650.0	59.32	451.1
300	370.85	1.023	652.3	60.00	452.3
350	429.64	1.020	713.9	80.03	485.3
400	484.57	1.017	774.9	102.90	517.7
450	534.74	1.016	834.9	128.40	549.6
500	580.01	1.015	893.7	156.29	581.1
550	620.68	1.014	950.9	186.33	612.1
600	657.9	1.013	1006.5	218.29	642.2
650	690.4	1.012	1060.4	251.97	672.7
700	719.71	1.012	1112.6	287.24	702.3
750	746.58	1.011	1163.2	323.91	731.4
800	771.00	1.011	1212.2	361.86	759.9
850	793.27	1.011	1259.6	400.97	787.9
900	813.62	1.010	1305.6	441.15	815.4
950	832.26	1.010	1350.1	482.31	842.4
1000	849.36	1.010	1393.2	524.35	868.8

#### 4. Specific Comments

The accuracy of the data employed for the calculations was commented on in Ref. 4 for the individual ions. The entropies at 298.15 K may be taken as generally having an uncertainty of two to ten times the unit of the last digit reported.<sup>3</sup> The other thermodynamic functions are no more accurate than this limit (except, of course,  $C_p/C_v$ ).

The following comments pertain to the tables marked with an asterisk.

Table 4:  $O_2^-$ . The ion is in its ground electronic state  $^2\Pi_{g1}$  at all temperatures of interest, the first excited state being<sup>9</sup> at 25 300 cm<sup>-1</sup>. The discrepancies between the tabulated and JANAF<sup>1</sup> values exceed the estimated error and are related to the difference in vibrational frequencies and interatomic distance used in the computation, ours being the more modern values of Ref. 9.

Table 9:  $VO^{2+}$ . The ground state of this  $3d^1$  ion is  $^2D_3$ , with  $J = 5/2$ . The first excited state is<sup>10</sup> at about 14 000 cm<sup>-1</sup>, and need not be taken into account at the temperatures of interest.

Table 9a:  $SbO^+$ . This ion was not included in the previous review.<sup>4</sup> The Sb-O bond length was taken as 0.1807 nm and the vibration frequency as 942 cm<sup>-1</sup>.<sup>11</sup>

Table 19:  $BO_2^-$ . The input data have not been specified in the previous review,<sup>4</sup> since the standard molar entropy at 298.15 K was taken from the review by Srivastava and Farber.<sup>12</sup> For the present calculations the B-O distance for this symmetrical linear ion was taken as 0.1291 nm, and the vibration frequencies were taken as  $\nu_1 = 1220$  cm<sup>-1</sup>,  $\nu_2 = 610$  cm<sup>-1</sup> (doubly degenerate), and  $\nu_3 = 2440$  cm<sup>-1</sup>. These values are consistent with both the  $S^\circ$  and  $C_p^\circ$  values given by Srivastava and Farber.<sup>12</sup> The discrepancies between the tabulated and JANAF<sup>1</sup> values which exceed the estimated error, are related to the small differences in vibrational frequencies and bond length used here<sup>12</sup> and those estimated for the JANAF tabulation.<sup>1</sup>

Table 23a:  $BrO_2^-$ . Although this ion was discussed in the previous review,<sup>4</sup> it was inadvertently not included in the

relevant table there but only in the text. Hence the vibrational frequencies employed were left out, and are now listed here for the sake of completeness:  $\nu_1 = 709$ ,  $\nu_2 = 324$ , and  $\nu_3 = 680$ , all in cm<sup>-1</sup>.<sup>13</sup>

Table 23b:  $AsO_2^-$ . This ion was not included in the previous review.<sup>4</sup> Solid meta-arsenites consist<sup>14</sup> of pyramidal  $AsO_3$  entities sharing corners, with an As-O bond length of 0.180 nm and O-As-O angles of 100 and 126°. For the isolated  $AsO_2^-$  ion, a bent structure was assumed, with the same As-O distance and with the mean value of the O-As-O angle. The Raman frequencies assigned to this ion are<sup>13</sup>  $\nu_1 = 753$  cm<sup>-1</sup>,  $\nu_2 = 350$  cm<sup>-1</sup>, and  $\nu_3 = 533$  cm<sup>-1</sup>. However, the value for the stretching frequency  $\nu_3$  seems to be too low, in view of the value reported<sup>15</sup> for the isoelectronic  $SeO_2$ . Replacement of this value by 800 cm<sup>-1</sup> as was done here, changes the entropy at 298.15 K by -1.5 J K<sup>-1</sup> mol<sup>-1</sup>.

Table 25a:  $NpO_2^{2+}$ . This ion was discussed only briefly in the previous review,<sup>4</sup> but was accorded a full treatment in a subsequent paper,<sup>5</sup> where the sources of the data were given and their selection was discussed. The calculations are based on the <sup>237</sup>Np isotope, on a symmetrical linear ion with an Np-O distance of 0.180 nm, and on the following vibrational frequencies:  $\nu_1 = 863$  cm<sup>-1</sup>,  $\nu_2 = 220$  cm<sup>-1</sup> (doubly degenerate), and  $\nu_3 = 934$  cm<sup>-1</sup>. The ground state for the odd electron has  $j = 5/2$ , the first excited level at 6752 cm<sup>-1</sup> has  $j = 7/2$ , but is not effectively involved in the temperature range of interest.

Table 25b:  $PuO_2^{2+}$ . The same general comment applies as for Table 25a. The calculations are based on the <sup>239</sup>Pu isotope, the Pu-O distance of 0.182 nm, the frequencies  $\nu_1 = 835$ ,  $\nu_2 = 220$ , and  $\nu_3 = 930$  cm<sup>-1</sup>, and on  $j = 4$  for the ground electronic state,  $j = 0$  for the first excited state at 2445 cm<sup>-1</sup>, and  $j = 1$  for the second one at 4258 cm<sup>-1</sup>, both of the latter making small contributions to the thermodynamic functions at the higher temperatures.

Table 25c:  $AmO_2^{2+}$ . The same general comment applies as for Table 25a. The calculations are based on the <sup>241</sup>Am isotope, the Am-O distance of 0.183 nm, the frequencies

$\nu_1 = 796$ ,  $\nu_2 = 216$ , and  $\nu_3 = 914 \text{ cm}^{-1}$ , and on  $j = 9/2$  for the ground electronic state. The first excited state at  $8889 \text{ cm}^{-1}$  is not of significance for the temperature range of interest.

Table 26:  $\text{UO}_2^+$ . The same general comment applies as for Table 25a. The calculations are based on the U-O distance of  $0.181 \text{ nm}$ , the frequencies  $\nu_1 = 759$ ,  $\nu_2 = 211$ , and  $\nu_3 = 892 \text{ cm}^{-1}$ , and on  $j = 5/2$  for the ground electronic state. The first excited state at  $6800 \text{ cm}^{-1}$  with  $j = 7/2$  is not significant for the temperature range of interest.

Table 26a:  $\text{NpO}_2^+$ . The same general comment applied as for Table 25a. The calculations are based on the  $^{237}\text{Np}$  isotope, the Np-O distance of  $0.183 \text{ nm}$ , the frequencies  $\nu_1 = 767$ ,  $\nu_2 = 186$ , and  $\nu_3 = 787 \text{ cm}^{-1}$ , and on  $j = 4$  for the ground electronic state,  $j = 0$  for the first excited state at  $2475 \text{ cm}^{-1}$ , and  $j = 1$  for the second one at  $3893 \text{ cm}^{-1}$ .

Table 26b:  $\text{PuO}_2^+$ . The same general comment applies as Table 25a. The calculations are based on the  $^{239}\text{Pu}$  isotope, the Pu-O distance of  $0.185 \text{ nm}$ , the frequencies  $\nu_1 = 748$ ,  $\nu_2 = 187$ , and  $\nu_3 = 792 \text{ cm}^{-1}$ , and on  $j = 9/2$  for the ground electronic state. The first excited state at  $8143 \text{ cm}^{-1}$  with  $j = 11/2$  is not contributing in the temperature range of interest.

Table 26c:  $\text{AmO}_2^+$ . The same general comment applies as for Table 25a. The calculations are based on the  $^{241}\text{Am}$  isotope, the Am-O distance of  $0.186 \text{ nm}$ , the frequencies  $\nu_1 = 730$ ,  $\nu_2 = 186$ , and  $\nu_3 = 788 \text{ cm}^{-1}$ , and on  $j = 1$  for the ground electronic state. No information is available on the low-lying excited states, hence the calculations provide only a lower limit for the thermodynamic functions. The systematics of the resulting values for the actinide-yl ions indicates<sup>5</sup> that some contribution from the excited electronic states should be expected.

Table 31:  $\text{AgI}_2^-$ . Only the linear configuration of this ion was used for the present calculations.

Table 56:  $\text{MnO}_4^{2-}$ . The ground state for the odd electron is  $^2\text{E}$ , with  $j = 3/2$ . The first excited state is at  $16\ 500 \text{ cm}^{-1}$ ,<sup>16</sup> and is not relevant at the temperature range of interest.

Table 67a:  $\text{Hg}(\text{CN})_4^{2-}$ . This ion was not included in the previous review.<sup>4</sup> It is regularly tetrahedral ( $T_d$ , symmetry number 12), with linear Hg-C-N groupings, Hg-C distances of  $0.222 \text{ nm}$  and C-N distances of  $0.115 \text{ nm}$  according to Griffiths.<sup>17</sup> The following vibration frequencies (in  $\text{cm}^{-1}$ ) have been adopted from Jones<sup>18</sup>:  $\nu_1 = 2148$ ,  $\nu_2 = 335$  (non-degenerate),  $\nu_3 = 245$ ,  $\nu_4 = 63$  (doubly degenerate),  $\nu_5 = 2146$ ,  $\nu_6 = 330$ ,  $\nu_7 = 235$ ,  $\nu_8 = 54$ , and  $\nu_9 = 180$  (triply degenerate). The lines corresponding to  $\nu_3$  and  $\nu_4$  are not observed in the spectra, but their frequencies were estimated by Jones.<sup>18</sup>

Table 76a:  $\text{AuBr}_4^-$ . This ion was not included in the previous review.<sup>4</sup> It is square planar ( $D_{4h}$ , symmetry number 8), with an Au-Br distance of  $0.257 \text{ nm}$  and the following vibration frequencies (in  $\text{cm}^{-1}$ ) according to Goggin and Mink<sup>19</sup>:  $\nu_1 = 214$ ,  $\nu_2 = 99$ ,  $\nu_3 = 196$ ,  $\nu_4 = 106$ ,  $\nu_5 = 61$  (non-degenerate),  $\nu_6 = 222$ , and  $\nu_7 = 106$  (doubly degenerate). The  $\nu_5$  vibration was not observed in the spectrum, and its frequency was estimated.<sup>19</sup>

Table 76b:  $\text{Ag}(\text{NH}_3)_2^+$ . This ion was not included in

the previous review.<sup>4</sup> According to Miles *et al.*<sup>20</sup> and to Geddes *et al.*,<sup>21</sup> it has a linear N-Ag-N grouping with Ag-N distances of  $0.188 \text{ nm}$ , and regular tetrahedral Ag-NH<sub>3</sub> groupings with N-H distances of  $0.103 \text{ nm}$ . The -NH<sub>3</sub> groups were not taken as rotating freely around the Ag-N bonds, since a torsion frequency has been assigned to the corresponding vibration. Hence the ion has a  $D_{3d}$  symmetry and a symmetry number of 6. The skeletal vibrations are at  $400$  and  $476 \text{ cm}^{-1}$  (Ag-N stretches) and  $211$  and  $221 \text{ cm}^{-1}$  (N-Ag-N bends), and the ammonia-group vibrations are at  $265 \text{ cm}^{-1}$  (torsion),  $648$  and  $653 \text{ cm}^{-1}$  (rockings, both doubly degenerate),  $1283$  and  $1300 \text{ cm}^{-1}$  (H-N-H bends), and further vibrations at  $> 1600 \text{ cm}^{-1}$ , which are of no concern for the present purpose.<sup>20,21</sup>

Table 77:  $\text{Pd}(\text{NH}_3)_4^{2+}$ . No values for possible torsion frequencies of the -NH<sub>3</sub> groups around the Pd-N bonds were reported. Free rotation of these groups around the bonds was therefore assumed for this ion. The uncertainty introduced in consequence was discussed in the previous review.<sup>4</sup>

Table 78:  $\text{Pt}(\text{NH}_3)_4^{2+}$ . Free rotation of the -NH<sub>3</sub> groups around the Pt-N bonds was assumed also for this ion, since no values for possible torsion frequencies were reported. The uncertainty introduced in consequence was discussed in the previous review.<sup>4</sup>

Table 102:  $\text{ReCl}_6^{3-}$ . The ground state for this  $5d^3$  ion  $^4\Gamma_2$  with  $j = 3/2$ . The first excited electronic state is at about  $14\ 500 \text{ cm}^{-1}$ ,<sup>22</sup> and is not significant at the temperature range of interest.

Table 104:  $\text{IrCl}_6^{2-}$ . The ground state of this  $5d^5$  ion is  $^2\text{T}_{2g}$  with  $j = 5/2$ . The first excited electronic state is at about  $17\ 000 \text{ cm}^{-1}$ , and is not significant in the temperature range of interest.<sup>23</sup>

Table 108:  $\text{Fe}(\text{CN})_6^{3-}$ . The ground state of this  $3d^5$  ion is  $^2\text{T}_{2g}$  with  $j = 5/2$ . No information was presented concerning the first excited electronic level, but it is expected to be located sufficiently high for it not be involved in the present calculations.<sup>23</sup>

Table 110:  $\text{Co}(\text{NH}_3)_6^{3+}$ . Free rotation of the -NH<sub>3</sub> groups around the Co-N bonds was assumed for this ion, in view of the absence of assigned values for torsion frequencies. Octahedral  $O_h$  symmetry, with a symmetry number of 24 was therefore assumed. The uncertainty introduced thereby was discussed in the previous review.<sup>4</sup>

Table 116:  $\text{CH}_3\text{SO}_3^-$ . This ion was not included in the previous review.<sup>4</sup> The structural data are from Wei and Hingerty<sup>24</sup> for the sodium salt: both parts of the ion are tetrahedral, with the regular tetrahedral angles for H-C-H and  $112.0^\circ$  and  $106.8^\circ$  for O-S-O and O-S-C ones, respectively. The average S-O bond distance is  $0.1448 \text{ nm}$ , the C-H one is  $0.097 \text{ nm}$ , and the S-C one is  $0.1754 \text{ nm}$ . Similar data were given for the silver and the cesium salts by Charbonnier *et al.*<sup>25</sup> and by Brandon and Brown.<sup>26</sup> Since there is spectroscopic evidence (see below) for hindered (rather than free) rotation around the C-S bond, the symmetry number was taken as 3. The vibration frequencies and their assignments are from a Raman spectroscopic study of an aqueous solution by Gillespie and Robinson,<sup>27</sup> and were confirmed by Raman and infrared studies by Miles *et al.*,<sup>28</sup> Burger *et al.*,<sup>29</sup>

and Campbell *et al.*<sup>30</sup> For the torsion mode  $\nu_6$ , however, the value obtained from nonelastic neutron scattering experiments by Ratcliffe *et al.*<sup>31</sup> was used. The frequencies in  $\text{cm}^{-1}$  are:  $\nu_1 = 2943$ ,  $\nu_2 = 1368$ ,  $\nu_3 = 1050$ ,  $\nu_4 = 778$ ,  $\nu_5 = 560$ ,  $\nu_6 = 261$  (nondegenerate),  $\nu_7 = 3020$ ,  $\nu_8 = 1435$ ,  $\nu_9 = 1177$ ,  $\nu_{10} = 960$ ,  $\nu_{11} = 533$ ,  $\nu_{12} = 344$  (doubly degenerate).

Table 117:  $\text{CF}_3\text{SO}_3^-$ . This ion was not included in the previous review.<sup>4</sup> The structural data are from Olofson *et al.*<sup>32,33</sup> for the hydronium salt (i.e., the monohydrated acid). Both parts of the ion are tetrahedral, with the regular tetrahedral angles for F-C-F and  $114.2^\circ$  and  $104.1^\circ$  for O-S-O and O-S-C ones, respectively. The average S-O bond distance is 0.1440 nm, the C-F one is 0.1312 nm, and the S-C one is 0.1825 nm. The symmetry number was taken as 3, as for the analogous  $\text{CH}_3\text{SO}_3^-$  ion, see comment on Table 116. The vibration frequencies and their assignments are from a Raman spectroscopic study of an aqueous solution by Miles *et al.*,<sup>28</sup> which were confirmed by Raman and infrared studies by Gansewein and Belim,<sup>34</sup> Burger *et al.*,<sup>29</sup> and Balycheva *et al.*<sup>35</sup> However, no value for the torsion mode  $\nu_6$  was reported, so that it was estimated to be  $65 \pm 15 \text{ cm}^{-1}$ , on the basis of the corresponding torsion frequencies of the acetate and trifluoroacetate anions, see the previous review.<sup>4</sup> The other frequencies used, in  $\text{cm}^{-1}$ , are:  $\nu_1 = 1230$ ,  $\nu_2 = 766$ ,  $\nu_3 = 1038$ ,  $\nu_4 = 321$ ,  $\nu_5 = 580$  (nondegenerate),  $\nu_7 = 1285$ ,  $\nu_8 = 520$ ,  $\nu_9 = 1188$ ,  $\nu_{10} = 208$ ,  $\nu_{11} = 635$ , and  $\nu_{12} = 353$  (doubly degenerate). The uncertainty caused by that in  $\nu_6$  amounts to  $\pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$  in the entropy at 298.15 K.

Table 118:  $\text{B}(\text{C}_6\text{H}_5)_4^-$ . This ion was not included in the previous review,<sup>4</sup> but was discussed in detail in the authors' subsequent paper,<sup>6</sup> where details of the structural data and the vibrational frequencies are given.

Table 119:  $(\text{C}_6\text{H}_5)_4\Gamma^+$ . See the comment on Table 118.

Table 120:  $(\text{C}_6\text{H}_5)_4\text{As}^+$ . See the comment on Table 118.

## 5. Acknowledgments

The authors wish to thank Dr. P. Tremaine who encouraged them to proceed with the publication of these tables. Support by the U.S.-Israel Binational Science Foundation, Grant No. 84-00292, is gratefully acknowledged.

## 6. References

- <sup>1</sup>D. R. Stull, *JANAF Thermochemical Tables*, 2nd ed. (U.S. GPO, Washington, D.C., 1971); *J. Phys. Chem. Ref. Data* **7**, 831 (1978); *J. Phys. Chem. Ref. Data* **11**, 695 (1982).
- <sup>2</sup>I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Springer, Berlin, 1973).
- <sup>3</sup>Y. Marcus and A. Loewenschuss, *Annual Reports C*, 1981 (Royal Soc. Chem. London, 1985), p. 81.
- <sup>4</sup>A. Loewenschuss and Y. Marcus, *Chem. Rev.* **84**, 89 (1984).
- <sup>5</sup>Y. Marcus and A. Loewenschuss, *J. Chem. Soc. Faraday Trans. 1* **82**, 2873 (1986).
- <sup>6</sup>Y. Marcus and A. Loewenschuss, *J. Chem. Soc. Faraday Trans. 1* **82**, 993 (1986).
- <sup>7</sup>G. A. Krestov, *Termodinamika Ionikh Protsessov v Rastvorakh* (Khimiya, Leningrad, 1984).
- <sup>8</sup>K. S. Pitzer and L. Brewer, *Thermodynamics*, 2nd ed. (McGraw-Hill, New York, 1961).
- <sup>9</sup>K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- <sup>10</sup>C. K. Jorgensen, *Acta Chem. Scand.* **11**, 73 (1957).
- <sup>11</sup>R. Tripathi, S. B. Bai, and K. N. Upadhyaya, *J. Phys. B* **14**, 441 (1981).
- <sup>12</sup>R. D. Srivastava and M. Farber, *Chem. Rev.* **78**, 627 (1978).
- <sup>13</sup>B. Sombret and F. Wallart, *C. R. Acad. Sci. Ser. B* **277**, 663 (1973).
- <sup>14</sup>F. Feher and G. Morgenstern, *Z. Anorg. Chem.* **232**, 169 (1937).
- <sup>15</sup>K. Nakamoto, *Vibration Spectra of Inorganic Compounds*, 3rd ed. (Wiley-Interscience, New York, 1977).
- <sup>16</sup>H. P. Gray, *Inorg. Chem.* **3**, 1115 (1964).
- <sup>17</sup>W. P. Griffiths, *Coord. Chem. Rev.* **17**, 177 (1975).
- <sup>18</sup>L. II. Jones, *Spectrochim. Acta* **17**, 188 (1961).
- <sup>19</sup>P. L. Goggin and J. Mink, *J. Chem. Soc. Dalton Trans.* **1479** (1974).
- <sup>20</sup>M. G. Miles, J. H. Patterson, C. W. Hobbs, M. J. Hooper, J. Overend, and R. S. Tobias, *Inorg. Chem.* **7**, 1721 (1968).
- <sup>21</sup>A. L. Geddes and G. L. Bottger, *Inorg. Chem.* **8**, 802 (1969).
- <sup>22</sup>C. K. Jorgensen, *Acta Chem. Scand.* **9**, 710 (1955).
- <sup>23</sup>C. K. Jorgensen, *Acta Chem. Scand.* **10**, 518 (1956).
- <sup>24</sup>C. H. Wei and B. E. Hingerty, *Acta Crystallogr. Sect. B* **37**, 1992 (1981).
- <sup>25</sup>F. Charbonnier, R. Faure, and H. Loiseleur, *Acta Crystallogr. Sect. B* **33**, 2824 (1977).
- <sup>26</sup>J. K. Brandon and I. D. Brown, *Can. J. Chem.* **45**, 1385 (1967).
- <sup>27</sup>R. J. Gillespie and E. A. Robinson, *Can. J. Chem.* **40**, 644 (1962).
- <sup>28</sup>M. G. Miles, G. Doyle, R. P. Cooney, and R. S. Tobias, *Spectrochim. Acta Part A* **25**, 1515 (1969).
- <sup>29</sup>H. Burger, K. Burczyk, and A. Blaschette, *Monatsh. Chem.* **101**, 102 (1970).
- <sup>30</sup>R. J. Campbell, K. H. Rhee, and K. S. Seshadri, *Spectrochim. Acta Part A* **24**, 955 (1968).
- <sup>31</sup>C. I. Ratcliffe, T. C. Waddington, and J. Howard, *J. Chem. Soc. Faraday Trans. 2* **78**, 1881 (1982).
- <sup>32</sup>R. G. Delaplane, J. O. Lundgren, and I. Olofson, *Acta Crystallogr. Sect. B* **31**, 2208 (1975).
- <sup>33</sup>J. O. Lundgren, R. Tellgren, and I. Olofson, *Acta Crystallogr. Sect. B* **34**, 2945 (1978).
- <sup>34</sup>B. Gansewein and H. Behm, *Z. Anorg. Allg. Chem.* **428**, 248 (1977).
- <sup>35</sup>T. G. Balycheva, V. I. Ligus, and Yu. Ya. Fialkov, *Zh. Neorg. Khim.* **18**, 3195 (1973).