

# Standard Thermodynamic Functions of Some Isolated Ions at 100–1000 K

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The standard thermodynamic functions ( $C_p^\circ$ ,  $S^\circ$ ,  $H^\circ$  and  $(G^\circ - H_0^\circ)/T$ ) at 100 to 1000 K of 24 polyatomic gaseous ions are reported, based on structural and spectroscopic data from the literature. These ions supplement the 130 ions previously studied and are: zirconyl, hydrotelluride, amide, selenocyanate, tellurocyanate, orthoborate, metaphosphate, arsenite, orthosilicate, tetrachloropalladate(II), tetrabromopalladate(II), tetrachloroplatinate(II), tetrabromoplatinate(II), hexafluorophosphate, hexafluoroarsenate, hexafluoroantimonate, hexabromoplatinate(IV), tetracyanonickelate, tetracyanomercurate, octacyanomolybdate(IV), sulfamate, benzoate, guanidinium, and glycine as cation, zwitterion, and anion. © 1996 American Institute of Physics and American Chemical Society.

Key words: bond lengths and angles; enthalpy of ions; entropy of ions; Gibbs energy function of ions; heat capacity of ions; isolated ions; thermodynamic functions; vibrational spectra.

## Contents

1. Introduction	1495	13. Thermodynamic functions for tetrabromoplatinate(II), $\text{PtBr}_4^{2-}$	1500
2. Results for Isolated Ions	1496	14. Thermodynamic functions for hexafluorophosphate, $\text{PF}_6^-$	1501
2.1. Diatomic Ions	1496	15. Thermodynamic functions for hexafluoroarsenate, $\text{AsF}_6^-$	1501
2.2. Triatomic Ions	1496	16. Thermodynamic functions for hexafluoroantimonate, $\text{SbF}_6^-$	1502
2.3. Tetraatomic Ions	1498	17. Thermodynamic functions for hexabromoplatinate(IV), $\text{PtBr}_6^{2-}$	1502
2.4. Pentaatomic Ions	1498	18. Thermodynamic functions for tetracyanonickelate, $\text{Ni}(\text{CN})_4^{2-}$	1502
2.5. Octahedral Heptaatomic Ions	1500	19. Thermodynamic functions for tetracyanomercurate, $\text{Hg}(\text{CN})_4^{2-}$	1503
2.6. More Complicated Ions	1502	20. Thermodynamic functions for octacyanomolybdate, $\text{Mo}(\text{CN})_8^{4-}$	1503
3. Discussion	1506	21. Thermodynamic functions for sulfamate, $\text{H}_2\text{NSO}_3^-$	1504
4. References	1506	22. Thermodynamic functions for benzoate, $\text{C}_6\text{H}_5\text{CO}_2^-$	1504
		23. Thermodynamic functions for guanidinium, $\text{C}(\text{NH}_2)_3^+$	1504
		24. Thermodynamic functions for glycine zwitterion, $^+\text{H}_3\text{NCH}_2\text{CO}_2^-$	1505
		25. Thermodynamic functions for glycinate, $\text{H}_2\text{NCH}_2\text{CO}_2^-$	1505
		26. Thermodynamic functions for glycinium, $^+\text{H}_3\text{NCH}_2\text{COOH}$	1506

## List of Tables

1. Thermodynamic functions for zirconyl ion, $\text{ZrO}^{2+}$	1496
2. Thermodynamic functions for hydrotelluride, $\text{HTe}^-$	1497
3. Thermodynamic functions for amide, $\text{NH}_2^-$	1497
4. Thermodynamic functions for selenocyanate, $\text{SeCN}^-$	1497
5. Thermodynamic functions for tellurocyanate, $\text{TeCN}^-$	1498
6. Thermodynamic functions for orthoborate, $\text{BO}_3^{3-}$	1498
7. Thermodynamic functions for metaphosphate, $\text{PO}_3^-$	1498
8. Thermodynamic functions for arsenite, $\text{AsO}_3^{3-}$	1499
9. Thermodynamic functions for orthosilicate, $\text{SiO}_4^{4-}$	1499
10. Thermodynamic functions for tetrachloropalladate(II), $\text{PdCl}_4^{2-}$	1499
11. Thermodynamic functions for tetrabromopalladate(II), $\text{PdBr}_4^{2-}$	1500
12. Thermodynamic functions for tetrachloroplatinate(II), $\text{PtCl}_4^{2-}$	1500

## 1. Introduction

The standard thermodynamic functions ( $C_p^\circ$ ,  $S^\circ$ ,  $H^\circ$  and  $(G^\circ - H_0^\circ)/T$ ) at 100 to 1000 K of more than 130 polyatomic gaseous ions were reported by us several years ago.<sup>1</sup> These were based on structural and vibration-spectroscopic data obtained from the literature (or estimated where necessary) and

summarized either in that publication, or in a previous one dealing with the entropies  $S^\circ$  at 298.15 K only.<sup>2</sup> We have now calculated such functions for an additional 24 polyatomic gaseous ions, based on similar data summarized and discussed in the present paper.

The explicit statistical-thermodynamic expressions required for the calculations were presented previously.<sup>1</sup> They were based on the ideal gas approximation and assume the separability of the translational, vibrational, and rotational degrees of freedom, hence the additivity of their contributions. The electronic contributions could be neglected for all the species considered here, since the ground state electronic level is not degenerate and excited levels are too high to contribute significantly. The ideal models of a rigid rotor and harmonic oscillator were used for the rotational and vibrational degrees of freedom. These assumptions may impose the upper temperature boundary of 1000 K to the validity of the calculations. The tabulated values pertain to the pressure of 0.101325 MPa, in order to conform to the previous publications.<sup>1,2</sup> Changing over to the standard pressure of 0.1 MPa increases the entropy and the Gibbs free energy function by  $R \ln 1.01325 = 0.109442 \text{ J K}^{-1} \text{ mol}^{-1}$  for all species and temperatures. The heat capacity and enthalpy are not affected.

As before, structural data, bond lengths and angles from (mainly x-ray) diffraction studies of crystalline compounds, are taken to represent the structure of the gaseous ions for the purpose of the calculation of the rotational contributions to the thermodynamic functions. The vibrational-spectroscopic data of species in solution (mainly from Raman spectroscopy), nearer in their nature to isolated ions, are preferred where available over those for ionic species in solids (from both Raman and infrared spectra), due to the latter being prone to solid state effects. These may be symmetry constraints imposed by the crystal lattice and polarization by neighboring counter-ions. The phase for which the spectroscopic data used for the calculation pertain is stated for each species.

The present choice of ions is being made with the view to supplementing the species of similar structures previously considered, but it is limited by the structural and even more so by the spectroscopic information available in the literature. For an  $N$ -atomic ion,  $3 \times N - 6$  vibrations are required for non-linear species and  $3 \times N - 5$  for linear species, although some are degenerate if a rotational axis of  $C_{n>2}$  characterizes the symmetry of the ion. This places a practical limit on the size of  $N$  that can be considered in calculations of this kind. The type of vibration (A, B, E or T) is indicated for describing the degeneracy (1, 1, 2, and 3, respectively), without giving more details of the assignment, since there is often not agreement among different authors. Free rotation of one part of the molecule against the other is assumed not to take place if there is experimental evidence for a frequency assigned to the torsional mode of the bond in question. Also, a configuration of maximal symmetry is selected, if it does not contradict structural (x-ray diffraction) data.

It is not claimed that the ions for which calculations are

TABLE 1. Thermodynamic functions for zirconyl ion,  $\text{ZrO}^{2+}$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{ mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{ mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{ mol}^{-1}$
100	29.11	1.400	199.34	2.91	170.25
150	29.24	1.397	211.16	4.37	182.05
200	29.74	1.388	219.63	5.84	190.43
250	30.54	1.374	226.35	7.35	196.96
273.15	30.96	1.367	229.07	8.06	199.57
298.15	31.41	1.360	231.80	8.84	202.16
300	31.44	1.360	232.00	8.90	202.34
350	32.29	1.347	236.91	10.49	206.94
400	33.03	1.336	241.27	12.12	210.96
450	33.66	1.328	245.20	13.79	214.55
500	34.19	1.321	248.77	15.49	217.80
550	34.62	1.316	252.05	17.21	220.76
600	34.98	1.312	255.08	18.95	223.50
650	35.28	1.308	257.89	20.71	226.04
700	35.54	1.305	260.52	22.48	228.41
750	35.75	1.303	262.98	24.26	230.63
800	35.93	1.301	265.29	26.05	232.73
850	36.08	1.299	267.47	27.85	234.71
900	36.21	1.298	269.54	29.66	236.58
950	36.32	1.297	271.50	31.47	238.37
1000	36.42	1.296	273.36	33.29	240.07

performed are necessarily stable in the gas phase; certainly not over the entire temperature range up to 1000 K. Such calculated values can still serve as the basis for calculations of solvation and reaction thermodynamics, and as such have been found valuable in the past.

## 2. Results for Isolated Ions

### 2.1 Diatomic Ions

(1) *Zirconyl*,  $\text{ZrO}^{2+}$ : Crystalline compounds expected to involve discrete  $\text{ZrO}^{2+}$  groups are possibly  $\text{ZrOF}_2$  and  $\text{ZrO}(\text{SbF}_6)_2$ . In the former,<sup>3</sup> distances  $r(\text{Zr-O}) = 0.204$  to  $0.226 \text{ nm}$  and a stretching frequency of the Zr-O bond of  $\nu = 864 \text{ cm}^{-1}$  were reported, while for the latter  $\nu = 877 \text{ cm}^{-1}$  was reported.<sup>4</sup> The sensitivity of the resulting thermodynamic functions to the variation in the frequency is negligible (0.2% in  $S^\circ$  at 1000 K), whereas variation of the distance has a somewhat larger effect (~1% in  $S^\circ$  at 1000 K). Table 1 reports the data for  $r = 0.204 \text{ nm}$  and  $\nu = 864 \text{ cm}^{-1}$ .

(2) *Hydrotelluride*,  $\text{TeH}^-$ : The distance  $r(\text{Te-H})$  is expected to be the sum of the single bond radii given by Pauling<sup>5</sup> as  $0.138 \text{ nm}$  for Te and  $0.030 \text{ nm}$  for H, i.e.,  $r = 0.168 \text{ nm}$ . The vibrational frequency of the bond was reported<sup>6</sup> as  $\nu = 1975 \text{ cm}^{-1}$  in solid  $(\text{C}_6\text{H}_5)_4\text{PTeH}$ . The thermodynamic functions are reported in Table 2. The vibrational contribution to the thermodynamic functions is negligibly small, so that any variation in it is of no consequence.

### 2.2 Triatomic Ions

(3) *Amide*,  $\text{NH}_2^-$ : Botschwina<sup>7</sup> calculated with high precision the structure and the vibrational spectrum of the isolated amide anion. The distances in this bent ion of  $C_{2v}$  symmetry

TABLE 2. Thermodynamic functions for hydrotelluride,  $\text{HTe}^-$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	29.10	1.400	175.39	2.89	146.53
150	29.10	1.400	187.19	4.34	158.25
200	29.10	1.400	195.56	5.80	166.58
250	29.11	1.400	202.06	7.25	173.05
273.15	29.13	1.399	204.64	7.93	175.62
298.15	29.15	1.399	207.19	8.65	178.16
300	29.16	1.399	207.37	8.71	178.34
350	29.26	1.397	211.87	10.17	182.82
400	29.45	1.393	215.79	11.64	186.70
450	29.70	1.389	219.27	13.11	190.13
500	30.02	1.383	222.42	14.61	193.20
550	30.38	1.377	225.29	16.12	195.99
600	30.77	1.370	227.95	17.65	198.54
650	31.16	1.364	230.43	19.19	200.90
700	31.55	1.358	232.76	20.76	203.10
750	31.93	1.352	234.95	22.35	205.15
800	32.29	1.347	237.02	23.95	207.08
850	32.63	1.342	238.99	25.58	208.89
900	32.95	1.338	240.86	27.22	210.62
950	33.24	1.334	242.65	28.87	212.26
1000	33.52	1.330	244.36	30.54	213.82

TABLE 4. Thermodynamic functions for selenocyanate,  $\text{SeCN}^-$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	30.69	1.372	203.90	2.93	174.56
150	35.23	1.309	217.16	4.58	186.65
200	39.86	1.264	227.95	6.46	195.66
250	43.40	1.237	237.24	8.54	203.07
273.15	44.69	1.229	241.15	9.56	206.13
298.15	45.87	1.221	245.11	10.70	209.24
300	45.95	1.221	245.40	10.78	209.46
350	47.82	1.210	252.63	13.13	215.12
400	49.25	1.203	259.11	15.56	220.22
450	50.41	1.198	264.98	18.05	224.87
500	51.40	1.193	270.34	20.59	229.15
550	52.27	1.189	275.28	23.19	233.13
600	53.05	1.186	279.86	25.82	236.83
650	53.76	1.183	284.14	28.49	240.31
700	54.41	1.180	288.15	31.19	243.58
750	55.00	1.178	291.92	33.93	246.68
800	55.54	1.176	295.49	36.69	249.62
850	56.03	1.174	298.87	39.48	252.42
900	56.49	1.173	302.09	42.30	255.09
950	56.90	1.171	305.15	45.13	257.65
1000	57.28	1.170	308.08	47.99	260.09

are  $r(\text{N-H})=0.1030$  nm, the angle  $\angle \text{HNH}=102.0^\circ$ , and the frequencies are 3107.5 (A), 3163.8 (A), and 1462.5 (A)  $\text{cm}^{-1}$ . The calculated thermodynamic functions are reported in Table 3. Due to the high frequencies (energies), the vibrational contributions to the thermodynamic functions are small. The uncertainty in the rotational contribution, due to a slightly larger  $\angle \text{HNH}=104^\circ$ ,<sup>8</sup> is also very small.

(4) *Selenocyanate*,  $\text{SeCN}^-$ : The structure of this linear ion, discussed by Nagarajan and Hariharan<sup>9</sup> with respect to

TABLE 3. Thermodynamic functions for amide,  $\text{NH}_2$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	33.26	1.333	152.46	3.33	119.31
150	33.26	1.333	165.94	4.99	132.79
200	33.28	1.333	175.51	6.65	142.36
250	33.39	1.332	182.95	8.32	149.78
273.15	33.48	1.330	185.91	9.09	152.73
298.15	33.61	1.329	188.84	9.93	155.64
300	33.63	1.328	189.05	9.99	155.85
350	34.00	1.324	194.26	11.68	160.99
400	34.49	1.318	198.83	13.40	165.45
450	35.06	1.311	202.93	15.13	169.40
500	35.68	1.304	206.65	16.90	172.96
550	36.33	1.297	210.08	18.70	176.19
600	37.03	1.290	213.27	20.54	179.16
650	37.74	1.283	216.27	22.40	181.90
700	38.47	1.276	219.09	24.31	184.47
750	39.21	1.269	221.77	26.25	186.87
800	39.96	1.263	224.32	28.23	189.14
850	40.71	1.257	226.77	30.25	191.29
900	41.45	1.251	229.12	32.30	193.33
950	42.17	1.246	231.38	34.39	195.28
1000	42.88	1.241	233.56	36.52	197.15

the vibrational spectrum, was taken from Sutton's tables<sup>10</sup>:  $r(\text{Se-C})=0.1709$  nm and  $r(\text{C-N})=0.1153$  nm. The frequencies<sup>9</sup> are those reported by Greenwood *et al.*: 2079 (A), 535 (A) and 426 (E)  $\text{cm}^{-1}$  for solid  $\text{KSeCN}$ .<sup>11</sup> The resulting thermodynamic functions are reported in Table 4. Since the (doubly degenerate) bending and the Se-C stretching frequencies are fairly low, the variability due to other reported frequencies in solid  $\text{KSeCN}$  ought to be considered. Ti and Kettle<sup>12</sup> reported 419 and 427  $\text{cm}^{-1}$  (bending) and 563  $\text{cm}^{-1}$  (Raman), and Bürger and Schmid<sup>13</sup> reported 420.5 and 430.7 (bending) and 563.4  $\text{cm}^{-1}$  (infrared). In comparison to the former set, the latter set of frequencies produces an  $S^\circ$  value larger by 0.24 and a  $C_p^\circ$  value larger by 0.25  $\text{J K}^{-1} \text{mol}^{-1}$  at 298.15 K. The differences are hardly significant.

(5) *Tellurocyanate*,  $\text{TeCN}^-$ : As was the case for selenocyanate, Nagarajan and Hariharan<sup>9</sup> quoted data by Sutton<sup>10</sup> and Greenwood *et al.*,<sup>11</sup> and no other data were found. The distances are  $r(\text{Te-C})=0.1904$  nm,  $r(\text{C-N})=0.1153$  nm and the frequencies are 2086 (A), 459(A), and 403 (E)  $\text{cm}^{-1}$  for  $\text{KTeCN}$ . The resulting thermodynamic functions are reported in Table 5.

Our previous publication<sup>2</sup> reported  $S^\circ$  (298 K) of cyanate as 218.9 and of thiocyanate as 232.5  $\text{J K}^{-1} \text{mol}^{-1}$ , arising from  $r(\text{O-C})=0.113$  and  $r(\text{C-N})=0.127$  nm (or, probably, vice versa) for cyanate and  $r(\text{S-C})=0.161$  and  $r(\text{C-N})=0.117$  nm. In view of other reported  $r(\text{C-N})$  values, 0.127 nm appears to be excessively large. The rotational partition function is not sensitive to the reversal of the O-C and C-N distance values in this case. If, instead, the values quoted by Nagarajan and Hariharan<sup>9</sup> from Sutton's tables<sup>10</sup> are used along with Greenwood's<sup>11</sup> frequencies, the entropies become 218.69 and 233.46  $\text{J K}^{-1} \text{mol}^{-1}$ , respectively.

TABLE 5. Thermodynamic functions for tellurocyanate, TeCN<sup>-</sup>

T K	C <sub>p</sub> <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	C <sub>p</sub> <sup>o</sup> /C <sub>v</sub> <sup>o</sup>	S <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup> kJ mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T J K <sup>-1</sup> mol <sup>-1</sup>
100	31.30	1.362	210.71	2.95	181.25
150	36.55	1.294	224.36	4.64	193.44
200	41.32	1.252	235.56	6.59	202.61
250	44.72	1.228	245.17	8.75	210.18
273.15	45.91	1.221	249.19	9.80	213.32
298.15	46.99	1.215	253.25	10.96	216.50
300	47.07	1.215	253.55	11.05	216.73
350	48.74	1.206	260.93	13.44	222.52
400	50.02	1.199	267.53	15.91	227.74
450	51.05	1.195	273.48	18.44	232.50
500	51.93	1.191	278.91	21.02	236.87
550	52.72	1.187	283.89	23.63	240.93
600	53.43	1.184	288.51	26.29	244.70
650	54.09	1.182	292.81	28.97	248.24
700	54.69	1.179	296.85	31.69	251.57
750	55.25	1.177	300.64	34.44	254.71
800	55.76	1.175	304.22	37.22	257.70
850	56.23	1.174	307.61	40.02	260.53
900	56.66	1.172	310.84	42.84	263.24
950	57.05	1.171	313.92	45.68	265.83
1000	57.41	1.169	316.85	48.55	268.31

TABLE 7. Thermodynamic functions for metaphosphate, PO<sub>3</sub><sup>-</sup>

T K	C <sub>p</sub> <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	C <sub>p</sub> <sup>o</sup> /C <sub>v</sub> <sup>o</sup>	S <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup> kJ mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T J K <sup>-1</sup> mol <sup>-1</sup>
100	34.44	1.318	222.44	3.34	189.11
150	38.66	1.274	237.12	5.16	202.82
200	43.96	1.233	248.97	7.23	212.94
250	49.20	1.203	259.34	9.56	221.23
273.15	51.48	1.193	263.80	10.72	224.66
298.15	53.82	1.183	268.41	12.04	228.14
300	53.99	1.182	268.74	12.14	228.39
350	58.19	1.167	277.39	14.94	234.80
400	61.77	1.156	285.40	17.95	240.64
450	64.78	1.147	292.86	21.11	246.05
500	67.29	1.141	299.81	24.42	251.09
550	69.37	1.136	306.33	27.83	255.83
600	71.11	1.132	312.44	31.35	260.30
650	72.56	1.129	318.19	34.94	264.54
700	73.78	1.127	323.61	38.60	268.58
750	74.81	1.125	328.74	42.31	272.43
800	75.69	1.123	333.60	46.08	276.11
850	76.45	1.122	338.21	49.88	279.63
900	77.09	1.121	342.60	53.72	283.02
950	77.66	1.120	346.78	57.59	286.27
1000	78.15	1.119	350.78	61.48	289.40

### 2.3. Tetraatomic Ions

(6) *Orthoborate*, BO<sub>3</sub><sup>3-</sup>: This planar, trigonal ion, of D<sub>3h</sub> symmetry, has distances<sup>5,14</sup> r(B-O)=0.136 nm. There are two A-type and two E-type vibrations, with a corresponding set of frequencies in solid borates:<sup>14</sup> 939 and 712 and 1285 and 604 cm<sup>-1</sup>, respectively. The resulting thermodynamic functions are reported in Table 6. The most recently published set of frequencies<sup>15</sup> (borate in KBr crystals) is 949 (A), 736 (A), 1222 and 1247 (E), and 582(E) cm<sup>-1</sup> (the

TABLE 6. Thermodynamic functions for orthoborate, BO<sub>3</sub><sup>3-</sup>

T K	C <sub>p</sub> <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	C <sub>p</sub> <sup>o</sup> /C <sub>v</sub> <sup>o</sup>	S <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup> kJ mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T J K <sup>-1</sup> mol <sup>-1</sup>
100	33.50	1.330	207.05	3.33	173.88
150	35.48	1.306	220.93	5.04	187.42
200	39.33	1.268	231.64	6.91	197.20
250	43.93	1.233	240.90	8.99	205.06
273.15	46.09	1.220	244.89	10.03	208.27
298.15	48.37	1.208	249.03	11.21	211.53
300	48.54	1.207	249.32	11.30	211.76
350	52.81	1.187	257.13	13.84	217.71
400	56.62	1.172	264.44	16.58	223.11
450	59.94	1.161	271.30	19.49	228.10
500	62.79	1.153	277.77	22.56	232.76
550	65.23	1.146	283.87	25.76	237.14
600	67.32	1.141	289.64	29.08	241.28
650	69.10	1.137	295.10	32.49	245.22
700	70.62	1.133	300.28	35.98	248.98
750	71.93	1.131	305.20	39.55	252.57
800	73.05	1.128	309.88	43.17	256.02
850	74.03	1.127	314.34	46.85	259.32
900	74.87	1.125	318.59	50.57	262.50
950	75.61	1.124	322.66	54.34	265.57
1000	76.26	1.122	326.55	58.13	268.53

former E-type vibration has lost its degeneracy due to constraints in the crystal). Using these causes only a slight change in the thermodynamic functions.

(7) *Metaphosphate*, PO<sub>3</sub><sup>-</sup>: This ion generally appears in condensed states, but it has sometimes been referred to in the literature as a discrete species. It has C<sub>3v</sub> symmetry, i.e., it is trigonal-pyramidal, with the angle ∠OPO being 110° and the bond length r(P-O)=0.176 nm.<sup>5</sup> A set of vibrational frequencies was reported by Nagarajan for solid metaphosphates:<sup>16</sup> 982 (A), 551 (A), 1029 (E), and 458 (E) cm<sup>-1</sup>. The resulting thermodynamic functions are reported in Table 7. No other data were found.

(8) *Arsenite*, AsO<sub>3</sub><sup>3-</sup>: This trigonal-pyramidal ion with symmetry C<sub>3v</sub> is stable in both the crystalline and solution states, and has a bond distance r(As-O)=0.184 nm with the angle ∠OAsO being 110°.<sup>5</sup> Two sets of vibrational frequencies have been published. Nagarajan<sup>16</sup> reported 752 (A), 340 (A), 680 (E) and 340 (E) cm<sup>-1</sup> whereas Loehr and Plane<sup>16(a)</sup> gave for these vibrations 770, 325, 815, and 265 cm<sup>-1</sup>, respectively. The latter set, from Raman spectra of aqueous solutions, yielded the thermodynamic functions reported in Table 8, the vibrational entropy being 2.5 J K<sup>-1</sup> mol<sup>-1</sup> larger and the vibrational heat capacity 0.9 J K<sup>-1</sup> mol<sup>-1</sup> lower at 298.15 K than for the former set of frequencies. These differences diminish with increasing temperatures.

### 2.4. Pentaatomic Ions

(9) *Orthosilicate*, SiO<sub>4</sub><sup>4-</sup>: This ion exists mainly in the condensed state, but has been referred to as an individual species in the literature, with tetrahedral symmetry (T<sub>d</sub>) and r(Si-O)=0.163 nm.<sup>17</sup> Two sets of vibration frequencies have been reported: Rawat *et al.*<sup>18</sup> gave 842 (A), 444 (E), 972 (T),

TABLE 8. Thermodynamic functions for arsenite,  $\text{AsO}_3^{3-}$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	40.60	1.258	231.49	3.51	196.54
150	47.83	1.210	249.38	5.72	211.33
200	53.67	1.183	263.96	8.27	222.74
250	58.68	1.165	276.49	11.08	232.29
273.15	60.74	1.159	281.78	12.46	236.77
298.15	62.77	1.153	287.19	14.00	240.32
300	62.91	1.152	287.57	14.12	240.61
350	66.38	1.143	297.54	17.36	248.06
400	69.16	1.137	306.59	20.75	254.83
450	71.39	1.132	314.87	24.26	261.06
500	73.17	1.128	322.49	27.88	266.84
550	74.60	1.125	329.53	31.57	272.23
600	75.76	1.123	336.08	35.33	277.29
650	76.71	1.122	342.18	39.15	282.06
700	77.50	1.120	347.89	43.00	286.57
750	78.15	1.119	353.26	46.89	290.85
800	78.71	1.118	358.33	50.82	294.91
850	79.17	1.117	363.11	54.76	298.79
900	79.57	1.117	367.65	58.73	302.50
950	79.91	1.116	371.96	62.72	306.05
1000	80.21	1.116	376.07	66.72	309.45

and  $540 \text{ (T) cm}^{-1}$ , whereas Mueller and Nagarajan<sup>19</sup> gave 819, 340, 956, and  $527 \text{ cm}^{-1}$ , respectively. The former, more recent set for a solid silicate, yielded the thermodynamic functions reported in Table 9. The difference between the lowest frequencies reported is of most significance for the calculated vibrational contribution to the thermodynamic functions. The latter set of frequencies provides  $3.8 \text{ J K}^{-1} \text{ mol}^{-1}$  more to the entropy and  $2.6 \text{ J K}^{-1} \text{ mol}^{-1}$  more to the heat capacity at 298.15 K.

TABLE 9. Thermodynamic functions for orthosilicate,  $\text{SiO}_4^{4-}$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	37.03	1.289	216.51	3.40	182.65
150	45.12	1.226	232.98	5.44	196.81
200	54.08	1.182	247.19	7.92	207.69
250	62.45	1.154	260.18	10.84	216.92
273.15	65.98	1.144	265.86	12.33	220.84
298.15	69.51	1.136	271.79	14.02	224.88
300	69.76	1.135	272.23	14.15	225.17
350	75.90	1.123	283.45	17.80	232.72
400	80.94	1.114	293.93	21.72	239.73
450	85.04	1.108	303.71	25.87	246.32
500	88.38	1.104	312.85	30.21	252.53
550	91.10	1.100	321.40	34.70	258.42
600	93.34	1.098	329.43	39.31	264.01
650	95.19	1.096	336.98	44.03	269.35
700	96.72	1.094	344.09	48.83	274.44
750	98.01	1.093	350.81	53.70	279.32
800	99.10	1.092	357.17	58.63	283.99
850	100.03	1.091	363.20	63.61	288.48
900	100.83	1.090	368.95	68.63	292.80
950	101.52	1.089	374.42	73.69	296.96
1000	102.11	1.089	379.64	78.78	300.97

TABLE 10. Thermodynamic functions for tetrachloropalladate(II),  $\text{PdCl}_4^{2-}$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	67.67	1.140	265.49	4.51	220.55
150	84.04	1.110	296.37	8.34	240.88
200	92.78	1.098	321.87	12.78	258.06
250	97.67	1.093	343.15	17.55	273.03
273.15	99.20	1.091	351.86	19.83	279.36
298.15	100.51	1.090	360.61	22.33	285.82
300	100.59	1.090	361.23	22.52	286.28
350	102.46	1.088	376.89	27.60	298.15
400	103.72	1.087	390.66	32.75	308.88
450	104.60	1.086	402.93	37.96	318.67
500	105.24	1.086	413.98	43.21	327.67
550	105.72	1.085	424.04	48.48	335.99
600	106.09	1.085	433.25	53.78	343.73
650	106.38	1.085	441.76	59.09	350.95
700	106.61	1.085	449.65	64.42	357.73
750	106.80	1.084	457.01	69.75	364.12
800	106.95	1.084	463.91	75.10	370.15
850	107.08	1.084	470.40	80.45	375.86
900	107.19	1.084	476.52	85.80	381.29
950	107.28	1.084	482.32	91.17	386.46
1000	107.36	1.084	487.82	96.53	391.40

(10) *Tetrachloropalladate(II)*,  $\text{PdCl}_4^{2-}$ : This square planar ion, with symmetry  $D_{4h}$ , has been studied by many authors. The bond distance is  $r(\text{Pd-Cl})=0.231 \text{ nm}$ .<sup>5</sup> One of the frequencies (generally designated as  $\nu_5$ , of B-type) is not active in either the Raman or the infrared spectra, whereas three frequencies appear in the Raman and three in the infrared spectra, with no coincidences, due to the existence of an inversion center. The most complete set (also for other tetrahalommetallates) was that given by Goggin and Mink:<sup>20</sup> 303 (A), 275 (B,  $\nu_2$ ), 164 (B)  $\text{cm}^{-1}$  from Raman spectra of aqueous  $\text{PdCl}_4^{2-}$ , and 150 (A), 317 (E) and 167 (E)  $\text{cm}^{-1}$  from infrared spectra of solid  $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{PdCl}_4$ , is used for the present calculations to generate the results shown in Table 10. The missing frequency is estimated, following the suggestion of Nakamoto,<sup>21</sup> as  $\nu_5 = \nu_2/2^{1/2} = 194 \text{ cm}^{-1}$ , which is consistent with earlier work<sup>2</sup> for similar octahedral species. Alternative sets of frequencies were reported by Hendra,<sup>22</sup> Durig and Nagarajan,<sup>23</sup> Perry *et al.*,<sup>24</sup> and Bosworth and Clark.<sup>25</sup> The difference in the entropy due to using these different sets of frequencies is up to  $7.5 \text{ J K}^{-1} \text{ mol}^{-1}$ , independent of the temperature. Due to the low frequencies involved, this uncertainty is quite significant and similar differences would be noted also in the other thermodynamic functions.

(11) *Tetrabromopalladate(II)*,  $\text{PdBr}_4^{2-}$ : This ion is completely analogous to the chloro-complex, with the bond distance  $r(\text{Pd-Br})=0.2444 \text{ nm}$  from x-ray diffraction data.<sup>26</sup> The frequency set given by Goggin and Mink<sup>20</sup>: 188 (A), 172 (B,  $\nu_2$ ), 102 (B)  $\text{cm}^{-1}$  from Raman spectra of aqueous  $\text{PdBr}_4^{2-}$  and 114 (A), 243 (E), and 104 (E)  $\text{cm}^{-1}$  from infrared spectra of solid  $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{PdBr}_4$ , was again employed for the calculations, with results shown in Table 11. The missing frequency was estimated as above:  $\nu_5 = \nu_2/2^{1/2}$

TABLE 11. Thermodynamic functions for tetrabromopalladate(II), PdBr<sub>4</sub><sup>2-</sup>

T K	C <sub>p</sub> <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	C <sub>p</sub> <sup>o</sup> /C <sub>v</sub> <sup>o</sup>	S <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup> kJ mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T J K <sup>-1</sup> mol <sup>-1</sup>
100	83.68	1.110	301.93	5.59	246.15
150	95.10	1.096	338.35	10.10	271.13
200	100.24	1.090	366.50	15.00	291.62
250	102.89	1.088	389.19	20.08	308.96
273.15	103.69	1.087	398.33	22.47	316.16
298.15	104.36	1.087	407.44	25.07	323.45
300	104.40	1.087	408.09	25.27	323.97
350	105.35	1.086	424.26	30.51	337.19
400	105.97	1.085	438.37	35.80	348.98
450	106.41	1.085	450.88	41.11	359.64
500	106.72	1.084	462.11	46.44	369.34
550	106.96	1.084	472.29	51.78	378.26
600	107.13	1.084	481.61	57.13	386.49
650	107.27	1.084	490.19	62.49	394.15
700	107.38	1.084	498.14	67.86	401.31
750	107.47	1.084	505.55	73.23	408.02
800	107.55	1.084	512.49	78.61	414.34
850	107.61	1.084	519.01	83.98	420.32
900	107.66	1.084	525.17	89.37	425.98
950	107.70	1.084	530.99	94.75	431.36
1000	107.74	1.084	536.51	100.14	436.48

TABLE 12. Thermodynamic functions for tetrachloroplatinate(II), PtCl<sub>4</sub><sup>2-</sup>

T K	C <sub>p</sub> <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	C <sub>p</sub> <sup>o</sup> /C <sub>v</sub> <sup>o</sup>	S <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup> kJ mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T J K <sup>-1</sup> mol <sup>-1</sup>
100	68.70	1.138	271.91	4.65	225.55
150	84.12	1.110	302.98	8.50	246.39
200	92.65	1.099	328.47	12.94	263.86
250	97.51	1.093	349.71	17.71	278.99
273.15	99.04	1.092	358.42	19.98	285.36
298.15	100.36	1.090	367.15	22.48	291.87
300	100.45	1.090	367.77	22.66	292.33
350	102.34	1.088	383.41	27.74	304.27
400	103.61	1.087	397.16	32.89	315.05
450	104.51	1.086	409.42	38.09	324.88
500	105.17	1.086	420.47	43.33	333.91
550	105.66	1.085	430.52	48.61	342.25
600	106.04	1.085	439.73	53.90	350.00
650	106.33	1.085	448.23	59.21	357.24
700	106.57	1.085	456.12	64.53	364.04
750	106.76	1.084	463.47	69.86	370.43
800	106.92	1.084	470.37	75.21	376.47
850	107.05	1.084	476.86	80.56	382.19
900	107.16	1.084	482.98	85.91	387.63
950	107.26	1.084	488.78	91.27	392.81
1000	107.34	1.084	494.28	96.64	397.75

= 117 cm<sup>-1</sup>. The difference in the entropy due to the different frequencies reported by Hendra,<sup>22</sup> Durig and Nagarajan,<sup>23</sup> Perry *et al.*,<sup>24</sup> and Bosworth and Clark<sup>25</sup> is up to 8.0 J K<sup>-1</sup> mol<sup>-1</sup>.

(12) *Tetrachloroplatinate(II)*, PtCl<sub>4</sub><sup>2-</sup>: This ion is also completely analogous to the palladium complex, with the bond distance r(Pt-Cl)=0.231 nm.<sup>5</sup> The frequency set given by Goggin and Mink:<sup>20</sup> 330 (A), 171 (B, ν<sub>2</sub>), 312 (B) cm<sup>-1</sup> from Raman spectra of aqueous PtCl<sub>4</sub><sup>2-</sup> and 147 (A), 309 and 325 (E), and 167 (E) cm<sup>-1</sup> from infrared spectra of solid [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>PtCl<sub>4</sub>, was again employed for the calculations, with results shown in Table 12. The missing frequency could be estimated as above: ν<sub>5</sub>=ν<sub>2</sub>/2<sup>1/2</sup>=121 cm<sup>-1</sup>. However, the value found<sup>20</sup> for the analogous and isoelectronic ion AuCl<sub>4</sub><sup>-</sup>, 112 cm<sup>-1</sup>, was preferred, since the central atom does not move in the mode in question, hence its mass does not affect the vibrational frequency. Indeed, the even lower value of ν<sub>5</sub>=71 cm<sup>-1</sup> was reported by Yeranov,<sup>27</sup> but this may well be a lattice mode. Alternative sets of frequencies reported by Hendra,<sup>22</sup> Durig and Nagarajan,<sup>23</sup> Perry *et al.*,<sup>24</sup> and Bosworth and Clark<sup>25</sup> cause differences in the entropy up to 10.0 J K<sup>-1</sup> mol<sup>-1</sup>.

(13) *Tetrabromoplatinate(II)*, PtBr<sub>4</sub><sup>2-</sup>: This ion is also completely analogous to the palladium complex, with the bond distance r(Pt-Br)=0.246 nm, obtained from the single bond differences Pt-Cl, Pd-Cl, and r(Br) - r(Cl).<sup>5</sup> The frequency set given by Goggin and Mink:<sup>20</sup> 208 (A), 106 (ν<sub>2</sub>, B), 194 (B) cm<sup>-1</sup> from Raman spectra of aqueous PtBr<sub>4</sub><sup>2-</sup> and 104 (A), 225 (E), and 112 (E) cm<sup>-1</sup> from infrared spectra of solid [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>PtBr<sub>4</sub>, was again employed for the calculations, with results shown in Table 13. The missing frequency was estimated as above: ν<sub>5</sub>=ν<sub>2</sub>/2<sup>1/2</sup>=88 cm<sup>-1</sup>. Alternative sets of frequencies reported by Hendra,<sup>22</sup>

Durig and Nagarajan,<sup>23</sup> Perry *et al.*,<sup>24</sup> and Bosworth and Clark<sup>25</sup> cause differences in the entropy of up to 8.7 J K<sup>-1</sup> mol<sup>-1</sup>.

## 2.5. Octahedral Heptaatomic Ions

(14) *Hexafluorophosphate*, PF<sub>6</sub><sup>-</sup>: This ion, with symmetry O<sub>h</sub>, has a bond distance r(P-F)=0.164 nm according to Gillespie and Robinson.<sup>28</sup> An older estimate, 0.158 nm,<sup>29</sup>

TABLE 13. Thermodynamic functions for tetrachloroplatinate(II), PtBr<sub>4</sub><sup>2-</sup>

T K	C <sub>p</sub> <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	C <sub>p</sub> <sup>o</sup> /C <sub>v</sub> <sup>o</sup>	S <sup>o</sup> J K <sup>-1</sup> mol <sup>-1</sup>	H <sup>o</sup> -H <sub>0</sub> <sup>o</sup> kJ mol <sup>-1</sup>	-(G <sup>o</sup> -H <sub>0</sub> <sup>o</sup> )/T J K <sup>-1</sup> mol <sup>-1</sup>
100	83.86	1.110	305.30	5.62	249.19
150	95.25	1.096	341.78	10.14	274.29
200	100.35	1.090	369.97	15.05	294.85
250	102.97	1.088	392.68	20.14	312.24
273.15	103.76	1.087	401.83	22.53	319.46
298.15	104.42	1.087	410.95	25.13	326.77
300	104.47	1.086	411.60	25.32	327.29
350	105.40	1.086	427.77	30.57	340.53
400	106.01	1.085	441.89	35.86	352.35
450	106.44	1.085	454.40	41.17	363.02
500	106.75	1.084	465.63	46.50	372.74
550	106.98	1.084	475.82	51.84	381.66
600	107.15	1.084	485.14	57.20	389.91
650	107.29	1.084	493.72	62.56	397.58
700	107.40	1.084	501.67	67.93	404.74
750	107.49	1.084	509.09	73.30	411.46
800	107.56	1.084	516.03	78.67	417.79
850	107.62	1.084	522.55	84.05	423.77
900	107.67	1.084	528.70	89.44	429.43
950	107.71	1.084	534.52	94.82	434.82
1000	107.75	1.084	540.05	100.21	439.95

TABLE 14. Thermodynamic functions for hexafluorophosphate,  $\text{PF}_6^-$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	41.02	1.254	224.73	3.48	190.07
150	57.63	1.169	244.32	5.92	204.95
200	76.04	1.123	263.45	9.27	217.22
250	92.16	1.099	282.21	13.49	228.37
273.15	98.53	1.092	290.65	15.69	233.30
298.15	104.65	1.086	299.55	18.24	238.49
300	105.07	1.086	300.20	18.43	238.87
350	115.08	1.073	317.18	23.94	248.88
400	122.79	1.073	333.07	29.90	258.43
450	128.75	1.069	347.89	36.19	267.57
500	133.40	1.066	361.71	42.75	276.31
550	137.08	1.065	374.60	49.52	284.68
600	140.03	1.063	386.66	56.45	292.69
650	142.42	1.062	397.97	63.51	300.36
700	144.37	1.061	408.60	70.68	307.73
750	145.99	1.060	418.61	77.94	314.80
800	147.34	1.060	428.08	85.28	321.59
850	148.48	1.059	437.05	92.67	328.13
900	149.45	1.059	445.56	100.12	334.42
950	150.28	1.059	453.66	107.62	340.49
1000	150.99	1.058	461.39	115.15	346.35

TABLE 15. Thermodynamic functions for hexafluoroarsenate,  $\text{AsF}_6^-$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	49.93	1.200	232.23	3.71	195.20
150	72.00	1.131	256.66	6.76	211.68
200	91.23	1.100	280.12	10.86	225.91
250	106.25	1.085	302.17	15.82	239.00
273.15	111.83	1.080	311.83	18.35	244.78
298.15	117.05	1.076	321.86	21.21	250.83
300	117.40	1.076	322.58	21.42	251.27
350	125.65	1.071	341.33	27.51	262.83
400	131.80	1.067	358.53	33.96	273.75
450	136.45	1.065	374.33	40.67	284.07
500	140.01	1.063	388.90	47.58	293.85
550	142.79	1.062	402.38	54.65	303.12
600	144.99	1.061	414.91	61.85	311.93
650	146.76	1.060	426.58	69.15	320.31
700	148.20	1.059	437.51	76.52	328.30
750	149.38	1.059	447.78	83.96	335.94
800	150.36	1.059	457.45	91.46	343.24
850	151.19	1.058	466.60	99.00	350.24
900	151.89	1.058	475.26	106.57	356.95
950	152.49	1.058	483.49	114.18	363.40
1000	153.01	1.057	491.32	121.82	369.61

appears to be too low in view of the sum of the reported single bond radii.<sup>5</sup> The set of vibrational frequencies given by Bougon *et al.*:<sup>30</sup> 746 (A,  $\nu_1$ ), 561 (E,  $\nu_2$ ), 475 (T,  $\nu_3$ ), from Raman spectra of solutions in HF and 817 (T,  $\nu_3$ ), 557 (T,  $\nu_4$ ), and 316 (T,  $\nu_6$ )  $\text{cm}^{-1}$  from infrared spectra of crystalline  $\text{ClO}_2^+\text{PF}_6^-$ , was used for the calculations, with results shown in Table 14.

The frequency  $\nu_6$ , that ought to be missing in a centrosymmetric ion, was nevertheless reported, because of slight deformation of the octahedron in the solid phase. However, the anion frequencies did not deviate much from solid to solution. If  $\nu_6$  is taken, as before,<sup>2,21</sup> as  $\nu_6 = \nu_5/2^{1/2} = 394 \text{ cm}^{-1}$ , then it agrees with the calculated assignment by Aleksandrovskaya *et al.*,<sup>31</sup>  $\nu_6 = 402 \text{ cm}^{-1}$ . The frequencies given by other authors<sup>29,32</sup> do not differ enough to produce significant changes in the thermodynamic functions, but the variation in  $\nu_6$  produces a difference in these functions, e.g., the entropy at 298.15 K is  $4.4 \text{ J K}^{-1} \text{mol}^{-1}$  larger with the smaller frequency value.<sup>30</sup>

(15) *Hexafluoroarsenate*,  $\text{AsF}_6^-$ : This ion is completely analogous to hexafluorophosphate, with the bond distance  $r(\text{As-F}) = 0.175 \text{ nm}$  being taken again from Gillespie and Robinson.<sup>28</sup>

The difference between this and the alternative,  $r(\text{As-F}) = 0.172 \text{ nm}$ <sup>32</sup> is insignificant, but the value  $0.182 \text{ nm}$  given by Begun and Rutenberg<sup>29</sup> is much too large, in view of the sum of the single bond radii.<sup>5</sup> The set of frequencies reported by Bougon *et al.*:<sup>30</sup> 682 (A,  $\nu_1$ ), 568 (E,  $\nu_2$ ), 369 (T,  $\nu_3$ ), 696 (T,  $\nu_3$ ), 379 (T,  $\nu_4$ ), and 248 (T,  $\nu_6$ )  $\text{cm}^{-1}$ , from Raman spectra of solutions and infrared spectra of solids as noted for  $\text{PF}_6^-$ , was again used for the calculations.

The value of  $\nu_6$  was only estimated, other estimates being  $263$ <sup>29</sup> and  $232$ <sup>31</sup>  $\text{cm}^{-1}$ , while the present estimate<sup>2,21</sup>  $\nu_6$

$= \nu_5/2^{1/2}$  is  $268 \text{ cm}^{-1}$ . The resulting thermodynamic functions are reported in Table 15. Other more or less complete sets of frequencies have been reported,<sup>29,31-33</sup> but as far as the thermodynamic functions are concerned, they differ significantly only with respect to  $\nu_6$ . The entropy at 298.15 K is  $1.7 \text{ J K}^{-1} \text{mol}^{-1}$  lower if  $268 \text{ cm}^{-1}$  is used for  $\nu_6$  instead of  $248 \text{ cm}^{-1}$ .

(16) *Hexafluoroantimonate*,  $\text{SbF}_6^-$ : This ion is analogous to the hexafluorophosphate and -arsenate ions, with a bond distance of  $r(\text{Sb-F}) = 0.1844 \text{ nm}$  according to Kruger *et al.*<sup>34</sup> This is essentially the same value as given by Begun and Rutenberg,  $0.1847 \text{ nm}$ .<sup>29</sup> Here also the frequency set of Bougon *et al.*:<sup>30</sup> 653 (A,  $\nu_1$ ), 561 (E,  $\nu_2$ ), 273 (T,  $\nu_3$ ), 667 (T,  $\nu_3$ ), 280 (T,  $\nu_4$ ) and 190 (T,  $\nu_6$ )  $\text{cm}^{-1}$ , as noted above for  $\text{PF}_6^-$ , was used for the calculations, with results shown in Table 16.

The uncertainty in  $\nu_6$  is again large, the minimal value being  $174 \text{ cm}^{-1}$  from the estimate by Aleksandrovskaya *et al.*<sup>32</sup> and the maximal value being  $252 \text{ cm}^{-1}$ , reported by Mohammed and Sherman,<sup>35</sup> for  $\text{SbF}_6^-$  isolated in a rubidium bromide crystal at a site symmetry of  $D_{2h}$ . The present estimate,  $\nu_6 = \nu_5/2^{1/2} = 197 \text{ cm}^{-1}$ , is consistent with the assignment of Bougon *et al.*<sup>32</sup> Most of the other frequencies reported<sup>29,31-33</sup> agree with the set of Bougon *et al.*,<sup>30</sup> also. These alternative values of  $\nu_6$  could produce a variation of  $8.5 \text{ J K}^{-1} \text{mol}^{-1}$  in the entropy, independent of the temperature, and corresponding changes in the other thermodynamic functions.

(17) *Hexabromoplatinate(IV)*,  $\text{PtBr}_6^{2-}$ : This octahedral ion, symmetry  $O_h$ , has a bond distance of  $r(\text{Pt-Br}) = 0.2481 \text{ nm}$  according to Grundy and Brown.<sup>36</sup> Essentially complete sets of frequencies have been reported by Debeau and Kransman,<sup>37</sup> Debeau and Poulet,<sup>38</sup> Pandey *et al.*,<sup>39</sup> and

TABLE 16. Thermodynamic functions for hexafluoroantimonate,  $\text{SbF}_6^-$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	63.02	1.152	243.12	4.18	201.38
150	85.51	1.108	273.14	7.93	220.41
200	102.37	1.088	300.17	12.64	237.06
250	115.00	1.078	324.44	18.09	252.17
273.15	119.68	1.075	334.83	20.81	258.75
298.15	124.03	1.072	345.50	23.80	265.59
300	124.33	1.072	346.27	24.09	266.09
350	131.20	1.068	365.98	30.48	278.99
400	136.31	1.065	383.85	37.18	291.01
450	140.17	1.063	400.14	44.10	302.26
500	143.13	1.062	415.07	51.18	312.81
550	145.43	1.061	428.82	58.40	322.75
600	147.25	1.060	441.56	65.72	332.14
650	148.71	1.059	453.40	73.12	341.02
700	149.90	1.059	464.47	80.58	349.46
750	150.88	1.058	474.84	88.10	357.48
800	151.69	1.058	484.61	95.67	365.13
850	152.38	1.058	493.83	103.27	372.44
900	152.95	1.057	502.55	110.90	379.43
950	153.45	1.057	510.84	118.56	386.14
1000	153.88	1.057	518.72	126.25	392.58

TABLE 18. Thermodynamic functions for tetracyanonickelate,  $\text{Ni}(\text{CN})_4^{2-}$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	83.84	1.110	289.37	5.90	230.44
150	106.85	1.084	327.78	10.68	256.69
200	125.36	1.071	361.19	16.51	278.75
250	138.37	1.064	390.65	23.12	298.27
273.15	142.93	1.062	403.11	26.38	306.64
298.15	147.07	1.060	415.81	30.01	315.28
300	147.35	1.060	416.72	30.28	315.90
350	153.78	1.057	439.95	37.82	332.01
400	158.67	1.055	460.81	45.63	346.84
450	162.64	1.054	479.74	53.67	360.58
500	166.04	1.053	497.05	61.89	373.39
550	169.08	1.052	513.02	70.27	385.38
600	171.84	1.051	527.86	78.79	396.65
650	174.39	1.050	541.71	87.45	407.29
700	176.76	1.049	554.72	96.23	417.37
750	178.94	1.049	567.00	105.12	426.94
800	180.96	1.048	578.61	114.12	436.07
850	182.82	1.048	589.64	123.21	444.79
900	184.54	1.047	600.14	132.40	453.14
950	186.12	1.047	610.16	141.66	461.14
1000	187.57	1.046	619.74	151.01	468.84

Berg,<sup>38</sup> with discrepancies regarding the assignment of the low frequencies ( $<150 \text{ cm}^{-1}$ ). The set by Debeau and Poulet:<sup>38</sup> 213 (A), 190 (E), 243 (T), 146 ( $\nu_4$ , T), 137 ( $\nu_5$ , T), 70 ( $\nu_6$ , T)  $\text{cm}^{-1}$  from Raman and infrared spectra of crystalline  $\text{K}_2\text{PtBr}_6$  was taken for the calculations with results shown in Table 17. The alternative<sup>39</sup> set of low frequencies, 90 (T,  $\nu_4$ ), 95 (T,  $\nu_5$ ),  $\nu_5/2^{1/2}=69$  (T,  $\nu_6$ )  $\text{cm}^{-1}$  produces entropy values  $21 \text{ J K}^{-1} \text{mol}^{-1}$  higher over the entire temperature range.

TABLE 17. Thermodynamic functions for hexabromoplatinate(IV),  $\text{PtBr}_6^{2-}$ 

T K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	114.98	1.078	327.79	7.01	257.79
150	134.97	1.066	378.76	13.33	290.00
200	144.05	1.061	418.98	20.33	317.43
250	148.74	1.059	451.68	27.66	341.14
273.15	150.16	1.059	464.92	31.12	351.09
298.15	151.36	1.058	478.13	34.89	361.20
300	151.43	1.058	479.06	35.17	361.93
350	153.11	1.057	502.54	42.79	380.39
400	154.22	1.057	523.06	50.47	396.98
450	154.99	1.057	541.27	58.21	412.04
500	155.55	1.056	557.64	65.97	425.80
550	155.96	1.056	572.48	73.76	438.48
600	156.28	1.056	586.07	81.56	450.23
650	156.53	1.056	598.58	89.39	461.18
700	156.72	1.056	610.19	97.22	471.42
750	156.88	1.056	621.01	105.06	481.04
800	157.02	1.056	631.14	112.90	490.12
850	157.12	1.056	640.66	120.76	498.70
900	157.21	1.056	649.65	128.62	506.85
950	157.29	1.056	658.15	136.48	514.59
1000	157.36	1.056	666.22	144.35	521.98

## 2.6. More Complicated Ions

(18) *Tetracyanonickelate (II)*,  $\text{Ni}(\text{CN})_4^{2-}$ : This is a square planar ion of symmetry  $D_{4h}$ , with bond lengths  $r(\text{Ni-C})=0.187 \text{ nm}$  and  $r(\text{C-N})=0.116 \text{ nm}$ .<sup>41</sup> A complete set of frequencies was reported by McCullough *et al.*<sup>42</sup> from the infrared spectrum of solid  $\text{Na}_2\text{Ni}(\text{CN})_4$ , including estimates for a few which remained unobserved. This set comprises 11 non-degenerate (A- and B-type) vibrations: 2149, 419, 325, 2141, 405, 488, (91), 448, (77), (303), and  $54 \text{ cm}^{-1}$  and 5 doubly-degenerate (E-type) vibrations: 2132, 543, 433, (78), and  $280 \text{ cm}^{-1}$ ; the estimated values are in parentheses. The resulting thermodynamic functions are shown in Table 18.

(19) *Tetracyanomercurate(II)*,  $\text{Hg}(\text{CN})_4^{2-}$ : This is a tetrahedral ion of symmetry  $T_d$ , with a bond length of  $r(\text{Hg-C})=0.222 \text{ nm}$ <sup>43</sup> (and  $r(\text{C-N})=0.116 \text{ nm}$ , as above). A complete set of frequencies was reported by Jones,<sup>43</sup> although, here too, a few had to be estimated, since they were not observed in their infrared spectrum of solid  $\text{K}_2\text{Hg}(\text{CN})_4$ . The frequencies are: 2149 (A), 335 (A), (245) (E), (63) (E), 2146 (T), 330 (T), 233 (T), 54 (T), and 180 (T)  $\text{cm}^{-1}$ , with estimated values in parentheses. The resulting thermodynamic functions are shown in Table 19.

(20) *Octacyanomolybdate(IV)*,  $\text{Mo}(\text{CN})_8^{4-}$ : The structure of this ion has been the subject of controversy. Earlier reports considered the aqueous ion to be an archimedean antiprism, of symmetry  $D_{4d}$ ,<sup>44,45</sup> based on vibration-spectroscopical evidence. The  $D_{4d}$  symmetry was also said to be consistent with <sup>13</sup>C NMR data in solution, in which the single line observed indicates that all the ligands are equivalent.<sup>46</sup> Later reports, however, considered the aqueous ion to be a dodecahedron, of  $D_{2d}$  symmetry.<sup>47,48</sup> All the authors agree that crystalline  $\text{K}_4\text{Mo}(\text{CN})_8 \cdot 2\text{H}_2\text{O}$  possesses the



TABLE 19. Thermodynamic functions for tetracyanomercurate,  $\text{Hg}(\text{CN})_4^{2-}$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	110.73	1.081	316.70	7.14	245.42
150	136.02	1.065	366.87	13.37	277.86
200	149.88	1.059	408.09	20.55	305.45
250	157.72	1.056	442.46	28.26	329.54
273.15	160.22	1.055	456.54	31.94	339.72
298.15	162.39	1.054	470.67	35.97	350.13
300	162.54	1.054	471.67	36.27	350.87
350	165.82	1.053	496.99	44.49	369.99
400	168.36	1.052	519.30	52.84	387.30
450	170.56	1.051	539.26	61.32	403.11
500	172.61	1.051	557.34	69.90	417.65
550	174.59	1.050	573.88	78.58	431.13
600	176.53	1.049	589.16	87.35	443.68
650	178.42	1.049	603.36	96.23	455.43
700	180.24	1.048	616.65	105.19	466.48
750	181.99	1.048	629.15	114.25	476.92
800	183.64	1.047	640.95	123.39	486.81
850	185.20	1.047	652.13	132.61	496.22
900	186.66	1.047	662.75	141.91	505.18
950	188.02	1.046	672.88	151.28	513.75
1000	189.28	1.046	682.56	160.71	521.96

TABLE 20. Thermodynamic functions for octacyanomolybdate,  $\text{Mo}(\text{CN})_8^{4-}$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	139.24	1.064	337.91	7.82	259.84
150	194.15	1.045	405.13	16.20	297.24
200	235.18	1.037	466.95	26.99	332.09
250	263.30	1.033	522.65	39.50	364.75
273.15	273.10	1.031	546.41	45.71	379.16
298.15	281.98	1.030	570.72	52.66	394.22
300	282.58	1.030	572.47	53.18	395.32
350	296.32	1.029	617.11	67.67	423.88
400	306.75	1.028	657.39	82.75	450.61
450	315.17	1.027	694.02	98.31	475.66
500	322.37	1.026	727.61	114.25	499.21
550	328.75	1.026	758.64	130.53	521.41
600	334.53	1.025	787.49	147.12	542.41
650	339.83	1.025	814.48	163.98	562.32
700	344.71	1.025	839.85	181.09	581.25
750	349.20	1.024	863.79	198.44	599.30
800	353.34	1.024	886.46	216.01	616.56
850	357.15	1.024	907.99	233.77	633.08
900	360.64	1.024	928.51	251.72	648.93
950	363.84	1.023	948.09	269.83	664.17
1000	366.78	1.023	966.83	288.10	678.84

$D_{2d}$  symmetry. This symmetry, on the other hand, is consistent with  $^{95}\text{Mo}$  NMR line widths in aqueous  $\text{Mo}(\text{CN})_8^{4-}$  containing solutions.<sup>49</sup> Suggestions concerning the isolated ("gaseous") ion  $\text{Mo}(\text{CN})_8^{4-}$  are also in disagreement:  $D_{4d}$ <sup>45</sup> and  $D_{2d}$ .<sup>47</sup>

The bond distances,  $r(\text{Mo}-\text{C})=0.2163$  and  $r(\text{C}-\text{N})=0.1156$  nm, and two sets of 4 angles  $\angle \text{CMoC}=69.1^\circ$  and  $145.6^\circ$ , were given in a paper reporting a complete set of calculated frequencies, for the  $D_{2d}$  (dodecahedron) symmetry.<sup>48</sup> These computed frequencies are in general agreement with the Raman and/or infrared spectra. These frequencies are: 2138, 2116, 568, 478, 419, 387, 331, 324, 152, 120, 116 (all A-type), 2117 (twice), 519, 486, 437, 381, 337, 328, 156, 133, 101, 52 (all B-type), 2116 (twice), 616, 463, 403, 362, 328, 321, 173, 136, 86 (all E-type, doubly degenerate)  $\text{cm}^{-1}$ . This information was considered by us the most reliable basis for the calculation of the thermodynamic functions shown in Table 20.

For the purpose of the calculation of thermodynamic functions, the configuration of the isolated ion is relevant to the rotational contributions with regard to the symmetry number: 4 for  $D_{2d}$  vs 8 for  $D_{4d}$  symmetries. The higher symmetry implies lower entropy and Gibbs function values by  $R \ln 2 = 5.8 \text{ J K}^{-1} \text{ mol}^{-1}$ .

(21) *Sulfamate*,  $\text{H}_2\text{NSO}_3^-$ : This ion was assigned a  $C_s$  symmetry, with the hydrogen atoms not being in the plane defined by the nitrogen, sulfur, and any of the oxygen atoms.<sup>51</sup> The set of distances and angles<sup>51</sup> obtained for  $\text{KH}_2\text{NSO}_3$ :  $r(\text{S}-\text{N})=0.1666$ ,  $r(\text{S}-\text{O})_{\text{mean}}=0.1457$ ,  $r(\text{N}-\text{H})_{\text{mean}}=0.1007$  nm,  $\angle \text{HNH}=110.2^\circ$ ,  $\angle \text{HNS}=110.2^\circ$ ,  $\angle \text{NSO}=116.1^\circ$ ,  $\angle \text{OSO}_{\text{mean}}=113.8^\circ$ , and  $\angle \text{SNO}=105.2^\circ$ , is used in the calculations. The free or hindered rotation of the  $-\text{NH}_2$  group with respect to the  $-\text{SO}_3$  group, is of significance

for the thermodynamic function calculations. For this ion, the barrier to free rotation was found to be high:  $1083^{52}$  or  $1370^{50} \text{ cm}^{-1}$  ( $1 \text{ cm}^{-1}=11.96 \text{ J mol}^{-1}$ ), so that a torsional vibration was assigned instead, at  $266 \text{ cm}^{-1}$ ,<sup>50</sup> in agreement with inelastic neutron scattering ( $267 \text{ cm}^{-1}$ ).<sup>53</sup> The other vibrational frequencies obtained for solid  $\text{KH}_2\text{NSO}_3$  are at: 3295, 3270, 1600, 1565, 1244, 1194, 1130, 1054, 995, 800, 594, 561, 406, and  $364 \text{ cm}^{-1}$  (all A-type),<sup>50</sup> in good agreement with the data of others.<sup>53-56</sup> The resulting thermodynamic functions are shown in Table 21.

It is of interest to compare the sulfamate ion with sulfamic acid, the zwitterion protonated form,  $^+\text{H}_3\text{NSO}_3^-$ . The rotational barrier is somewhat lower,  $945^{57}$  or  $953^{52} \text{ cm}^{-1}$ , leading to a somewhat lower torsional frequency,  $250 \text{ cm}^{-1}$  at 300 K ( $275 \text{ cm}^{-1}$  at 74 K).<sup>57,58</sup> The extra hydrogen atom is responsible for an additional stretching frequency ( $\sim 3200 \text{ cm}^{-1}$ ) and two additional bending frequencies ( $\sim 1000$  and  $\sim 1600 \text{ cm}^{-1}$ ). These high frequencies have little effect on the thermodynamic functions. However, the greater bond length  $r(\text{S}-\text{N})=0.1764 \text{ nm}$ <sup>52</sup> does make a difference in the symmetric stretching frequency (678 instead of  $809 \text{ cm}^{-1}$ ) and to the rotational contributions to these functions (the other structural data are nearly the same). Also, the symmetry number of the  $C_{3v}$  zwitterion is 3 rather than 1 of the anion, leading to  $R \ln 3=9.1 \text{ J K}^{-1} \text{ mol}^{-1}$  lower entropy and Gibbs function.

(22) *Benzoate*,  $\text{C}_6\text{H}_5\text{CO}_2^-$ : this flat symmetrical ion has symmetry  $C_{2v}$ . The relevant distances,  $r(\text{C}-\text{C})_{\text{ar}}=0.1397$ ,  $r(\text{C}-\text{C})=0.1504$ ,  $r(\text{C}-\text{O})=0.125$ , and  $r(\text{C}-\text{H})=0.1084$  nm, and the angles, which are all  $120^\circ$  except  $\angle \text{OCO}=125.5^\circ$ , are from Pauling,<sup>5</sup> the carboxylate group being planar with the phenyl ring. A complete set of frequencies (except for the torsional mode) was given by Green:<sup>59</sup>  $3073-3036$  (triplet),

TABLE 21. Thermodynamic functions for sulfamate,  $\text{H}_2\text{NSO}_3^-$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	38.38	1.277	230.89	3.44	196.63
150	46.57	1.217	247.97	5.56	211.03
200	55.04	1.178	262.53	8.10	222.15
250	63.29	1.151	275.70	11.06	231.58
273.15	67.02	1.142	281.47	12.57	235.57
298.15	70.95	1.133	287.51	14.29	239.69
300	71.23	1.132	287.95	14.42	239.98
350	78.72	1.118	299.50	18.17	247.68
400	85.61	1.108	310.47	22.28	254.86
450	91.84	1.100	320.92	26.72	261.64
500	97.39	1.093	330.89	31.46	268.08
550	102.32	1.088	340.40	36.45	274.24
600	106.69	1.085	349.50	41.68	280.14
650	110.57	1.081	358.19	47.11	285.82
700	114.03	1.079	366.52	52.73	291.30
750	117.13	1.076	374.49	58.51	296.59
800	119.92	1.074	382.14	64.44	301.70
850	122.45	1.073	389.49	70.50	306.66
900	124.74	1.071	396.55	76.68	311.46
950	126.83	1.070	403.35	82.97	316.13
1000	128.75	1.069	409.91	89.36	320.66

TABLE 22. Thermodynamic functions for benzoate,  $\text{C}_6\text{H}_5\text{CO}_2^-$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	50.84	1.195	254.43	3.92	215.30
150	65.26	1.146	277.71	6.82	232.36
200	81.76	1.113	298.69	10.48	246.37
250	99.89	1.091	318.86	15.02	258.88
273.15	108.53	1.083	328.09	17.43	264.37
298.15	117.86	1.076	337.99	20.26	270.13
300	118.54	1.075	338.72	20.48	270.56
350	136.68	1.065	358.37	26.87	281.72
400	153.61	1.057	377.74	34.13	292.53
450	169.03	1.052	396.74	42.20	303.07
500	182.85	1.048	415.28	51.01	313.37
550	195.18	1.044	433.30	60.46	323.47
600	206.14	1.042	450.76	70.50	333.36
650	215.92	1.040	467.65	81.06	343.06
700	224.66	1.038	483.98	92.08	352.55
750	232.51	1.037	499.75	103.51	361.85
800	239.58	1.036	514.99	115.31	370.95
850	245.98	1.035	529.71	127.46	379.87
900	251.79	1.034	543.93	139.90	388.59
950	257.08	1.033	557.69	152.63	397.14
1000	261.91	1.033	571.00	165.60	405.51

1595, 1488, 1413, 1172, 1150, 1026, 1006, 974, 845, 840, 680, 400, 397 (all of A-type), and 3088 (twice), 1595, 1552, 1413, 1305, 1301, 1157, 1065, 985, 919, 819, 709, 683, 617, 526, 418, 238, and 170 (all of B-type)  $\text{cm}^{-1}$  from the infrared spectrum in KCl disks and Nujol mulls, and confirmed by the Raman spectrum where possible. This set was more or less confirmed by other authors,<sup>60-62</sup> with deviations that are of no consequence for the thermodynamic functions. The torsional frequency was taken as 139  $\text{cm}^{-1}$  from the data for nitrobenzene,<sup>63</sup> since the nitrobenzene molecule is similar to the isoelectronic and isostructural benzoate anion. This assignment is confirmed by its presence in the Raman, but not in the infrared, spectrum of nitrobenzene.<sup>64</sup> The resulting thermodynamic functions are shown in Table 22.

(23) *Guanidinium*,  $\text{C}(\text{NH}_2)_3^+$ : This planar trigonal ion has symmetry  $D_{3h}$ , all the angles are  $120^\circ$ , and the bond distances are  $r(\text{C-N})=0.133$  and  $r(\text{N-H})=0.100$  nm.<sup>65</sup> The published sets of vibrational frequencies are incomplete, since three A-type vibrations are inactive in both the Raman and infrared spectra. The reported frequencies<sup>66</sup> derived from both kinds of spectra in aqueous solution (Raman) and crystalline chloride salt (infrared) are: 3340, 1625, 1015, 725, and 520 (all A-type), 3400, 3320, 1670, 1565, 1140, 536, 830, and 500 (all E-type)  $\text{cm}^{-1}$ , in good agreement with other reports.<sup>67-69</sup> The missing frequencies are assignable to C-N-H bending,  $\text{NH}_2$  rocking, and N-H stretching, with estimated frequencies of 500, 1100, and 3300  $\text{cm}^{-1}$ , respectively, in analogy with the reported active frequencies for these internal coordinates. A variation of up to 20% in the estimated frequencies causes changes in the entropy and Gibbs function that do not exceed 1-2  $\text{J K}^{-1} \text{mol}^{-1}$ . The resulting thermodynamic functions are shown in Table 23.

(24) *Glycine zwitterion*,  $^+\text{H}_3\text{NCH}_2\text{CO}_2^-$ : This form of gly-

cine, in the crystalline state and present in aqueous solutions at a pH range that envelops the isoelectric point,  $\text{pH}=6.0$ , is considered to have  $C_s$  symmetry in the isolated form. According to theoretical calculations,<sup>71</sup> the barriers to free internal rotation of the  $-\text{NH}_3$  and the  $-\text{CO}_2$  groups are high: 878 or 2341  $\text{cm}^{-1}$  (two alternative energies: 10.5 or 28.0  $\text{J K}^{-1} \text{mol}^{-1}$  having been suggested according to two basis sets) for the former and 4197  $\text{cm}^{-1}$  (50.2  $\text{J K}^{-1} \text{mol}^{-1}$ ) for the latter. The bond distances are  $r(\text{C-N})=0.147$ ,  $r(\text{C-C})$

TABLE 23. Thermodynamic functions for guanidinium,  $\text{C}(\text{NH}_2)_3^+$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	34.98	1.312	208.93	3.35	175.55
150	42.97	1.240	224.42	5.27	189.38
200	54.57	1.180	238.34	7.70	199.92
250	66.72	1.142	251.82	10.74	208.98
273.15	72.18	1.130	257.97	12.35	212.88
298.15	77.89	1.119	264.54	14.22	216.94
300	78.31	1.119	265.02	14.37	217.24
350	89.04	1.103	277.91	18.55	225.01
400	98.84	1.092	290.45	23.26	232.42
450	107.72	1.084	302.62	28.42	239.56
500	115.74	1.077	314.39	34.01	246.47
550	123.00	1.072	325.77	39.99	253.17
600	129.58	1.069	336.75	46.30	259.69
650	135.59	1.065	347.37	52.93	266.04
700	141.10	1.063	357.62	59.85	272.22
750	146.20	1.060	367.53	67.04	278.26
800	150.92	1.058	377.12	74.47	284.14
850	155.32	1.057	386.40	82.12	289.89
900	159.44	1.055	395.40	89.99	295.51
950	163.29	1.054	404.12	98.06	301.01
1000	166.90	1.052	412.59	106.32	306.38

TABLE 24. Thermodynamic functions for glycine zwitterion,  ${}^+\text{H}_3\text{NCH}_2\text{CO}_2^-$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	40.01	1.262	235.32	3.52	200.27
150	48.12	1.209	253.02	5.71	215.04
200	57.30	1.170	268.10	8.35	226.48
250	67.01	1.142	281.92	11.45	236.23
273.15	71.64	1.131	288.06	13.06	240.37
298.15	76.69	1.122	294.55	14.91	244.65
300	77.07	1.121	295.03	15.05	244.96
350	87.18	1.105	307.67	19.16	253.04
400	97.05	1.094	319.96	23.77	260.65
450	106.42	1.085	331.94	28.86	267.92
500	115.19	1.078	343.61	34.40	274.92
550	123.29	1.072	354.97	40.36	281.69
600	130.76	1.068	366.03	46.72	288.27
650	137.62	1.064	376.77	53.43	294.68
700	143.92	1.061	387.20	60.47	300.92
750	149.72	1.059	397.33	67.81	307.02
800	155.06	1.057	407.16	75.43	312.98
850	159.97	1.055	416.71	83.31	318.81
900	164.51	1.053	425.99	91.42	324.51
950	168.70	1.052	435.00	99.76	330.10
1000	172.57	1.051	443.75	108.29	335.57

$=0.152$ ,  $r(\text{C-O})=0.127$ ,  $r(\text{C-H})=0.109$ , and  $r(\text{N-H})=0.103$  nm, the angles are  $\angle \text{OCO}=122^\circ$ ,  $\angle \text{C(N)CO}=119^\circ$ , and the rest are tetrahedral,  $109.47^\circ$ .<sup>70</sup> A complete set of vibration frequencies (except for the five N-H and C-H stretching frequencies), both observed in and calculated for the Raman and infrared spectra of solid glycine, was reported by Machida *et al.*<sup>71</sup> The following data are the observed (calculated) values for the Raman spectrum in aqueous solution: 1669, 1642, 1570, 1513, 1441, 1410, 1324, (1328), 1139, (1108), 1034, (920), 890, 695, 603, 495, (472), 356, and 194  $\text{cm}^{-1}$ . The  $-\text{NH}_3$  torsion frequency is 472, the  $-\text{CO}_2$  torsion frequency is 194  $\text{cm}^{-1}$ . The not-reported stretching frequencies are all  $>3000 \text{ cm}^{-1}$ , hence of no consequence for the thermodynamic functions. This set,<sup>71</sup> used for our calculations, is in good agreement with other results.<sup>72-75</sup> The several low frequencies reported for the crystalline state are probably lattice modes.<sup>72</sup> The 110  $\text{cm}^{-1}$  frequency observed in the solid was assigned to the  $-\text{CO}_2$  torsion, instead of the unassigned, 194 frequency,<sup>72</sup> which we preferred (and used) because it was more consistent with the other assignments.<sup>72</sup> Raman spectra of the aqueous solutions<sup>74,75</sup> are in good agreement with data for the solid. A value for the  $-\text{NH}_3$  torsion obtained from inelastic neutron scattering,<sup>73</sup> 527  $\text{cm}^{-1}$ , is somewhat higher than calculated<sup>71</sup> for the Raman (472  $\text{cm}^{-1}$ ) and infrared (486  $\text{cm}^{-1}$ ) spectra, but has little effect on the thermodynamic functions. The thermodynamic functions calculated from the data presented above are shown in Table 24.

Deprotonation of glycine in solutions more basic than the isoelectric point produces the *glycinate anion*,  $\text{H}_2\text{NCH}_2\text{CO}_2^-$ . Its structure should not differ much from that of glycine, the effects on the thermodynamic functions

TABLE 25. Thermodynamic functions for glycinate,  $\text{H}_2\text{NCH}_2\text{CO}_2^-$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	39.93	1.263	234.81	3.51	199.78
150	47.98	1.210	252.47	5.70	214.54
200	57.03	1.171	267.50	8.33	225.97
250	66.50	1.143	281.23	11.41	235.68
273.15	70.96	1.133	287.32	13.01	239.81
298.15	75.80	1.123	293.74	14.84	244.07
300	76.16	1.123	294.21	14.98	244.38
350	85.72	1.107	306.67	19.03	252.41
400	94.87	1.096	318.72	23.55	259.96
450	103.41	1.087	330.40	28.51	267.16
500	111.24	1.081	341.70	33.88	274.06
550	118.36	1.076	352.65	39.62	280.72
600	124.82	1.071	363.23	45.70	287.17
650	130.68	1.068	373.45	52.09	293.42
700	136.00	1.065	383.33	58.76	299.50
750	140.85	1.063	392.89	65.68	305.42
800	145.29	1.061	402.12	72.84	311.18
850	149.34	1.059	411.05	80.20	316.80
900	153.07	1.057	419.69	87.77	322.28
950	156.49	1.056	428.06	95.51	327.64
1000	159.64	1.055	436.17	103.41	332.87

would therefore be small. The slightly lower ionic mass diminishes the translational entropy by  $1.5 R \ln(75/74)$ , i.e., by  $0.17 \text{ J K}^{-1} \text{mol}^{-1}$ . The absence of the light hydrogen atom rotating at  $\sim 0.2$  nm from the center of gravity of the molecule/ion lowers the rotational entropy by  $0.52 \text{ J K}^{-1} \text{mol}^{-1}$ . The set of vibration frequencies presented for this ion in aqueous solution is: 1603, 1454, 1430, 1405, 1346, 1316, 1168, 1110, 1082, 970, 905, 678, 587, and 516  $\text{cm}^{-1}$  is quite similar to that for glycine. This set is not only short of the required complement by the 2 C-H and 2 N-H stretching frequencies ( $>3200 \text{ cm}^{-1}$ ) which are of no consequence for the calculated thermodynamic functions, but also by 3 of the lower frequencies, which have to be estimated. Two of these should be the torsions of the  $-\text{NH}_2$  and  $-\text{CO}_2$  groups, which we take here to be the same as for glycine. The 359  $\text{cm}^{-1}$  frequency (assigned in glycine to CCN bending and  $\text{CO}_2$  rocking)<sup>75</sup> should not be affected by the absence of one hydrogen on the nitrogen atom. The thermodynamic functions for the glycinate anion calculated with this tentative set are shown in Table 25.

Similar arguments pertain to the protonated glycine in solutions more acidic than the isoelectric point, producing the *glycinium ion*,  ${}^+\text{H}_3\text{NCH}_2\text{COOH}$ . The increase in the mass raises the translational entropy by  $0.17 \text{ J K}^{-1} \text{mol}^{-1}$ . Again, on the assumption that the structure does not change appreciably except for addition<sup>70</sup> of  $r(\text{O-H})=0.097$  nm and  $\angle \text{COH}=120^\circ$ , the rotation of the extra hydrogen atom at  $\sim 0.3$  nm from the center of gravity is expected to add  $0.36 \text{ J K}^{-1} \text{mol}^{-1}$  to the rotational entropy. The set of vibrational frequencies reported<sup>75</sup> for aqueous solutions is: 1745, 1628, 1513, 1440, 1418, 1327, 1268, 1135, 1048, 903, 878, 655, 573, 509, 313  $\text{cm}^{-1}$ , and is again short of the expected number, even with the stretching frequencies (3 N-H, 2 C-H, and

TABLE 26. Thermodynamic functions for glycinium,  ${}^+\text{H}_3\text{NCH}_2\text{COOH}$ 

$T$ K	$C_p^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$C_p^\circ/C_v^\circ$	$S^\circ$ $\text{J K}^{-1} \text{mol}^{-1}$	$H^\circ - H_0^\circ$ $\text{kJ mol}^{-1}$	$-(G^\circ - H_0^\circ)/T$ $\text{J K}^{-1} \text{mol}^{-1}$
100	41.47	1.251	236.30	3.55	200.90
150	50.61	1.197	254.82	5.85	215.93
200	60.27	1.160	270.69	8.62	227.70
250	70.56	1.134	285.23	11.89	237.79
273.15	75.53	1.124	291.69	13.58	242.09
298.15	81.01	1.114	298.54	15.53	246.55
300	81.41	1.114	299.05	15.68	246.87
350	92.48	1.099	312.43	20.03	255.30
400	103.35	1.087	325.49	24.93	263.27
450	113.74	1.079	338.27	30.36	270.91
500	123.47	1.072	350.76	36.29	278.29
550	132.50	1.067	362.96	42.69	285.44
600	140.84	1.063	374.85	49.53	292.41
650	148.52	1.059	386.43	56.77	299.20
700	155.61	1.056	397.70	64.37	305.85
750	162.14	1.054	408.66	72.32	312.34
800	168.17	1.052	419.32	80.58	318.71
850	173.74	1.050	429.69	89.13	324.94
900	178.89	1.049	439.76	97.95	331.04
950	183.60	1.047	449.57	107.01	337.03
1000	188.07	1.046	459.10	116.31	342.90

1 O-H) excluded. The missing frequencies have to be estimated: for the torsions of  $-\text{NH}_3$  and  $-\text{CO}_2\text{H}$  are taken the glycine values, and twice  $\sim 1500$  and twice  $\sim 1000$  are added. The resulting calculated thermodynamic functions are shown in Table 26.

### 3. Discussion

The results presented in this work are an extension of our efforts<sup>1,2</sup> to provide thermodynamic functions for a variety of ionic species based upon critically reviewed structural and spectroscopic data. Such quantities, beyond being of interest in their own right, provide essential data for the evaluation of changes in thermodynamic quantities in the solvation processes in which such ions may be involved. This *rationale* guided us in the choice of ions discussed and also in the preference of solution data over those obtained from solid phase spectroscopic or structural analyses. It might be argued that the presented data are for a reference state of *isolated single ions* rather than for the ionic species as they actually exist in the gas phase at the relevant temperatures.

The latter remark pertains mostly to the disregard of free internal rotation in our considerations, even at the higher end of the temperature range. In the great majority of cases such attitude is also justified by physical considerations: the classical text by Brewer and Pitzer<sup>76</sup> states that free internal rotation is said to be of significance when the potential barrier is considerably lower than  $695 \text{ cm}^{-1}$ , the value of  $k \cdot T$  at 1000 K.

In several cases a symmetrical structure was chosen even if the possibility of slight deviations from it was indicated by the relevant literature pertaining to diffraction results in solid compounds. We checked the sensitivity of our results to the

effect of such deviations and adopted this attitude when we found the geometrical effects to be rather small (less than 1%). However, a reduction of symmetry may well involve a reduction in the symmetry number and appropriate change in the rotational contribution to the calculated thermodynamic functions. Again we feel that the higher symmetry may be more appropriate for the consideration of isolated ions or ions in solution. Moreover, the question what size of deviation (and at what temperature and barrier) justifies a postulation of a lowered symmetry is more of a philosophical nature and beyond the scope of this contribution.

In considering the structural and spectroscopic data we often had to decide between several (and sometimes conflicting) sets, especially where vibrational frequency values and assignments are concerned. Having made our choice of the most reasonable set of values, the ones from which the functions are tabulated, we also indicate the uncertainty involved, if other sets of similar reliability were to be chosen. When an alternative set greatly deviates from the one chosen for the calculations in the tables, we quote the relevant data and estimate the variation they would impose in the calculated value, but also indicate in the accompanying text that we regard these data to be of lower validity. In ascertaining the effects of variations in frequencies and assignments on the presented entropy values, our previously published table on the dependence of the calculated vibrational contributions on the frequency values and temperature should be useful.<sup>2</sup>

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