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The Entropies of Polyatomic Gaseous Ions

AHARON LOEWENSCHUSS and YIZHAK MARCUS*

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

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Contents

I.	Introduction	89
II.	Theoretical Basis for the Calculations	89
III.	Calculated Entropies	91
	A. Diatomic Ions	91
	B. Triatomic Ions	92
	C. Tetraatomic Ions	95
	D. Pentaatomic Ions	96
	1. MO_4^{n-}-Type Ions	97
	2. Other Regular-Tetrahedral Ions	99
	3. Other Pentaatomic Ions	100
	E. Hexaatomic Ions	102
	F. Ions of the Type X_2Y_n ($n \geq 4$)	103
	G. Octahedral Ions	106
	H. Miscellaneous Ions	109
IV.	References	112

I. Introduction

Entropies of gaseous ions may be considered as valuable quantities in themselves, but are also of interest in connection with their hydration properties.[1] For obtaining the latter, the standard entropies of the ions in the two standard states (aqueous), $\bar{S}_i^\infty(aq)$, and (gaseous), $S_i^\circ(g)$, are required.[2,3]

The entropies $S_i^\circ(g)$ for monatomic gaseous ions are generally equated with their translational entropies obtained from the Sackur–Tetrode equation (1) at the

$$S_i^\circ{}_{tr} = R(1.5 \ln M_i + 2.5 \ln T) - 9.686 \text{ J K}^{-1} \text{ mol}^{-1} \tag{1}$$

standard pressure of 0.101 325 MPa, where R is the gas constant, M_i is the molar mass of the ion in g mol^{-1} (or the relative molar mass in atomic mass units, amu), and T is the temperature in K. Corrections for spin multiplicity may be required for some of the ions. Accurate values of $S_i^\circ(g)$ are generally available for most gaseous monatomic ions, e.g., in ref 2.

Not so are the entropies of gaseous polyatomic ions, which have been calculated on the basis of statistic mechanical equations for about four dozen of the more symmetrical ions only.[4-7] These calculations have been based on the best values of the molecular geometry and internuclear distances and the vibrational frequencies available at the time, most of which have by now been superseded by more accurate values. There are many more ions for which such data exist at present, but their entropies have so far not been calculated.

This review deals primarily with those polyatomic ions for which values of $\bar{S}_i^\infty(aq)$ are available. Excluded are complex ions that are labile in aqueous solutions, except for those where values of $S_i^\circ(g)$ have previously been reported. Included are some ions not classified as complex ions, for which $\bar{S}_i^\infty(aq)$ values are not available, but which are closely related to the other ions dealt with. The ions are classified mainly according to the number n of atoms they contain, up to $n = 5$. Beyond this number two general classes are considered: ions of the type X_2Y_m ($m \geq 4$) and octahedral ions, XY_6, where Y may be polyatomic itself. A small group of miscellaneous ions with $n \geq 6$ closes the list. The literature has been examined to the end of 1981.

II. Theoretical Basis for the Calculations

For polyatomic ions there are two contributions to the entropy in addition to the translational entropy $S_i^\circ{}_{tr}$ given by eq 1: a rotational contribution, $S_i^\circ{}_{rot}$, and a vibrational one, $S_i^\circ{}_{vib}$. For nonlinear ions they take the following form[8]

$$S_i^\circ{}_{rot} = R(0.5 \ln D + 1.5 \ln T - \ln \sigma) + 34.904 \text{ J K}^{-1} \text{ mol}^{-1} \tag{2}$$

where D is the determinant of the moments of inertia, and σ is the symmetry number. The coordinates x_j, y_j, and z_j of all the n atoms j with masses m_j in the n-atom ion are taken with the origin at the center of mass of the ion, and the following set of moments of inertia are calculated

$$I_x = \sum^n m_j(y_j^2 + z_j^2) \qquad I_y = \sum^n m_j(x_j^2 + z_j^2)$$
$$I_z = \sum^n m_j(x_j^2 + y_j^2) \qquad I_{xy} = \sum^n m_j x_j y_j \tag{3}$$
$$I_{xz} = \sum^n m_j x_j z_j \qquad I_{yz} = \sum^n m_j y_j z_j$$

The determinant is then

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Aharon Loewenschuss is Senior Lecturer at the Department of Inorganic and Analytical Chemistry of the Hebrew University of Jerusalem. He was born in 1937 in Czernowitz, Romania, and immigrated to Israel in 1948. He obtained his Ph.D. from Technion, Israel Institute of Technology, in Haifa in 1967. In 1968 he received a Bath Sheba de Rothschild Fellowship for Young Scientists and then spent 2 years at U.C.L.A. doing postdoctoral work on light scattering from liquids. Following this he returned to his present position where his research interests lie in the field of molecular spectroscopy with emphasis on the matrix isolation method. In 1978 he went to the U.S. for a sabbatical year at the University of Virginia and Marquette University. As a recipient of an Alexander von Humboldt fellowship he spent several research periods at the Universities of Bielefeld and Kaiserslautern. He has authored some 40 research papers.

Yizhak Marcus was born in Kolberg, Germany, in 1931, and immigrated to Israel in 1936. He obtained the M.Sc. and Ph.D. degrees in 1952 and 1956 from the Hebrew University of Jerusalem. He returned after postdoctoral research in Sweden and the U.S.A. to the Soreq Nuclear Research Center in Israel in 1958, to work on the actinides and on ion-exchange and solvent-extraction separations. On his appointment in 1965 as Professor at the Hebrew University, he served until 1973 as Head of the Inorganic and Analytical Chemistry Department. His research interests range from molten salts through aqueous and nonaqueous electrolytes to mixtures of organic liquids. He has published some 130 research papers and two books, on ion exchange and solvent extraction (with A. S. Kertes) and on liquid-state chemistry. He held a Senior Alexander von Humboldt Fellowship (1971–1976), and has served on IUPAC bodies in various capacities since 1963.

$$D = I_xI_yI_z - 2I_{xy}I_{yz}I_{xz} - I_xI_{yz}^2 - I_yI_{xz}^2 - I_zI_{xy}^2 \quad (4)$$

For symmetrical molecules, however, the cartesian axes can be readily chosen so that the cross-terms in the moments of inertia, i.e., I_{xy}, I_{xz}, and I_{yz}, are all zero (the principal axes of inertia), and then $D = I_xI_yI_z$. Equation 2 is valid with the numerical term shown, provided the atomic masses are in amu (or g mol^{-1}) and the coordinates in nm (i.e., D is in amu^3 nm^6). The symmetry number σ is the number of indistinguishable positions into which the ion can be turned by simple rigid rotations. E.g., for a bent triatomic XY_2-type ion of C_{2v} symmetry $\sigma = 2$, for a pyramidal ion of C_{3v} symmetry $\sigma = 3$, for a planar trigonal ion belonging to symmetry group D_{3h} $\sigma = 6$, for a tetrahedral ion of symmetry group T_d $\sigma = 12$, and for a octahedral ion of symmetry group O_h $\sigma = 24$.

The vibrational contribution to the entropy is given by the sum

$$S_i°_{\text{vib}} = R\sum_1^N[u(e^u - 1)^{-1} - \ln(1 - e^{-u})] \quad (5)$$

where N is the number of vibrational degrees of freedom, which for an n-atom nonlinear ion equals $3n - 6$, and

$$u = (1.4387/T)(\nu/\text{cm}^{-1}) \quad (6)$$

where ν is the vibration frequency (degeneracies are included in the summation).

For a linear ion one rotational degree of freedom is transformed into a vibrational one, so that $N = 3n - 5$. The rotational contribution to the entropy is then[8]

$$S_i°_{\text{rot(lin)}} = R(1 - \ln y - \ln \sigma - y^2/90) \quad (7)$$

where

$$y = 0.242\,54\ (I/(\text{amu nm}^2))^{-1}\ T^{-1} \quad (8)$$

$I = {}^n\sum m_jx_j^2$ is the moment of inertia, with distances x_j along the axis of the ion measured from its center of mass. The symmetry number is $\sigma = 2$ for a symmetrical linear ion and $\sigma = 1$ for a nonsymmetrical one.

If a polyatomic part A of the ion can rotate around a bond to the polyatomic residual part B of the ion, two situations can be distinguished.[8] If the potential energy barrier to the rotation is low enough at the temperature of interest so that $kT \gg hc\nu_{\text{tors}}$ (k is Boltzmann's constant and h is Planck's constant, c is the speed of light in cm s^{-1}, and ν_{tors} is the torsional frequency around this bond, in cm^{-1}), the degree of freedom is considered as a free internal rotation, and contributes to the entropy

$$S°_{\text{free rot}} = R(0.5 \ln I_r - \ln \sigma' + 0.5 \ln T) + 14.803\ \text{J K}^{-1}\ \text{mol}^{-1} \quad (9)$$

where $I_r = I_AI_B/(I_A + I_B)$ is the reduced moment of inertia in amu·nm^2, and I_A and I_B are the moments of inertia of the parts A and B rotating around the bond. The symmetry number σ, pertains to identical orientations for rotation around this bond. In this case of free internal rotation, the group A may be regarded as a single "heavy atom" with the mass of group A located at its center of mass, for both the calculations of $S_i°_{\text{rot}}$ and the evaluation of the symmetry number σ for the entire ion.

If, however, the torsional wavenumber ν_{tors} is sufficiently low, no free internal rotation can take place, and the motion is treated as a true (torsional) vibration. Then, the relative orientation of parts A and B is fixed, and the symmetry of the ion is lowered (in some cases to an extent that $\sigma = 1$ results).

The expressions given above for $S_i°_{\text{rot}}$ and $S_i°_{\text{vib}}$ are approximations, adequate for the present purposes at the temperature $T = 298.15$ K. They are based on the consideration of the ion as a rigid rotator (apart from internal rotations) and of the normal modes as harmonic oscillators. Also, summations over the quantum numbers are replaced by integrals. A correction for anharmonicity and for centrifugal forces can be calculated for diatomic ions, if the parameters α (relating the mean interatomic distance with the vibrational energy) and x (relating to the difference in vibrational energy between the ground and first excited states) are known.[8] This correction is

$$\Delta S = R[2xu(e^u - 1)^{-2}(1 + (2ue^u - e^u + 1)/(e^u - 1)] + (hc/kT)\alpha_y{}^{-1}(e^u - 1)(1 + ue^u/(e^u - 1)) + 16yu^{-2}] \quad (10)$$

where the other quantities have already been defined. Sample calculations for a few diatomic molecules and ions show that the correction at room temperature is not very significant: for Cl_2 ΔS/J K^{-1} mol^{-1} is 0.34, for OH^- it is 0.039, for O_2^- it is 0.033, and for others even smaller.

The calculated $S_i°(g)$ values in this review are all for T = 298.15 K. Should entropy values for other temperatures be desired, then 33.26 ln (T/298.15) J K^{-1} mol^{-1} should be added to the sum of the translational and rotational contributions at 298.15 K, and the vibrational contributions must be reevaluated. For this purpose values for each vibrational degree of freedom may be interpolated from Table X in the Appendix. Alternatively, the vibrational contribution may be recalculated by using eq 5 and 6.

It should also be mentioned that there may be a temperature independent contribution to $S_i°(g)$ due to non-zero spin or orbital momentum in the ground electronic state. The spin multiplicity contribution to the entropy from a single unpaired electron is R ln 2.

Summarizing the foregoing, one sees that in order to apply eq 1, 2 or 7, and 5 to the calculation of $S_i°(g)$ the following input information is required. Needed are the number n of atoms in the ion, the masses m_j of these atoms and the pertinent bond lengths and angles, as well as the $3n - 6$ (or, for linear ions, $3n - 5$) vibrational frequencies. From the primary geometric structural data the coordinates x_j, y_j, and z_j of the atoms are calculated, and the symmetry of the ion is derived. The latter determines the symmetry number σ and the existence of degeneracies (i.e., coinciding values) among the vibrational frequencies. The calculations are generally based on the assumption that geometries, distances, and frequencies observed in condensed phases do not differ significantly from those valid for the gaseous ions. In fact, if the entropies of the gaseous ions are required solely for the calculation of entropies of hydration, it is preferable to use quantities pertaining to the ions in condensed phases (e.g., aqueous solutions), in order to avoid the need to include explicitly changes in the ionic configuration upon hydration. Some comments on these points have already been made in ref 4, 5, and 9.

III. Calculated Entropies

A. Diatomic Ions

The data for the diatomic ions, for most of which $\bar{S}_i^\infty(aq)$ data are available, are collected in Table I. For most of these ions entropy data have been published previously, but for some $S_i°(g)$ is given here for the first time, namely for ClO^-, BrO^-, VO^{2+}, S_2^{2-}, and Hg_2^{2+}. Following are comments on these data, the sources of the input data, and a comparison with previously published values. The sensitive input parameters (apart from the molar masses of the ions) are the interatomic distances r and the vibrational frequency ν (for values <1500 cm^{-1}). An uncertainty of 0.001 nm in the former causes an uncertainty of 0.017 $(r/\text{nm})^{-1}$ J K^{-1} mol^{-1} in $S_i°(g)$, and an uncertainty of 10 cm^{-1} in the latter causes uncertainties of 0.82, 0.10, and 0.02 J K^{-1} mol^{-1} in $S_i°(g)$ at ν = 200, 500, and 1000 cm^{-1}, respectively.

TABLE I. Standard Entropies of Gaseous Diatomic Ions at 298.15 K

no.	ion	r, nm	ν, cm^{-1}	$S_{tr}{}^a$	$S_{rot}{}^a$	$S_{vib}{}^a$	$S_i°(g)^a$
1	OH^-	0.0970	3700	144.1	28.2	0.0	172.3
2	SH^-	0.1341	2592	152.4	33.8	0.0	186.2
3	SeH^-	0.196	1708	163.4	40.3	0.0	203.8
4	O_2^-	0.1341	1090	152.0	45.7	0.3	203.8[b]
5	O_2^{2-}	0.149	1081	152.0	47.3	0.3	199.6
6	ClO^-	0.1570	713	157.9	56.6	1.2	215.7
7	BrO^-	0.1717	620	165.7	59.8	1.7	227.2
8	NO^+	0.1063	2376	151.0	47.2	0.0	198.4
9	VO^{2+}	0.167	985	161.2	58.5	0.4	225.9[b]
10	CN^-	0.1172	2069	149.4	47.3	0.0	196.7
11	S_2^{2-}	0.213	451	160.6	59.2	3.3	223.1
12	Hg_2^{2+}	0.296	180	183.5	79.8	9.7	273.0

[a] Units = J K^{-1} mol^{-1}. [b] The sum includes R ln 2 = 5.76 J K^{-1} mol^{-1} as the contribution of the electronic spin multiplicity.

1. **Hydroxide, OH^-.** The interatomic distance r is taken from the Huber and Herzberg compilation,[10] as is the vibrational frequency, but the latter is immaterial, since the vibrational contribution, S_{vib}, is negligible. The estimated uncertainty of $S_i°(g)$ is therefore ±0.2 J K^{-1} mol^{-1}, due to an uncertainty of ±0.001 nm in r. The value given by Altschuler,[5] 161 J K^{-1} mol^{-1}, is too low, that estimated from the isoelectronic HF by Vasilev,[6] 174 J K^{-1} mol^{-1}, is too high.

2. **Hydrosulfide, SH^-.** The values of r and ν are from ref 10, and the uncertainty in r leads to an uncertainty of ±0.2 J K^{-1} mol^{-1} in $S_i°(g)$. Krestov[7] gives an estimate of 187 J K^{-1} mol^{-1}, based on the isoelectronic HCl, and another of 193 J K^{-1} mol^{-1}, based on the "real distribution of charged species", the former being in better agreement with the present value.

3. **Hydroselenide, SeH^-.** The value of r is from Johnson (1973),[11] that of ν from ref 10. The uncertainty in r is rather large, since in ref 10 a value smaller by 0.048 nm is given, leading to $S_i°(g)$ smaller by 4.7 J K^{-1} mol^{-1}. Krestov,[7] again, gives one value, 199 J K^{-1} mol^{-1}, based on the isoelectronic HBr, which is in agreement with the present value, and another, 205 J K^{-1} mol^{-1}, based on the "real distribution of charged species", which is larger.

3a. **Hydrotelluride, TeH^-.** No value of $S_i°(g)$ is given for this ion, since no adequate source for r and ν data has been found. Krestov[7] gives the estimate 207 J K^{-1} mol^{-1} based on the isoelectronic HI, and the value 213 J K^{-1} mol^{-1}, based on the "real distribution of charged species".

4. **Superoxide, O_2^-.** The values of r and ν are from ref 10, the former has a relatively large uncertainty, estimated at ±0.002 nm, leading to an uncertainty of ±0.1 J K^{-1} mol^{-1} in $S_i°(g)$, whereas the uncertainty in ν (values from 1074 to 1097 cm^{-1} have been published) is immaterial. Altschuler[5] uses a considerably smaller value of r, but with an uncertainty of ±0.006 nm, omits the contribution of the spin multiplicity, and obtains $S_i°(g)$ = 197 ± 1 J K^{-1} mol^{-1}. Krestov[7] gives the value

TABLE II. Standard Entropies of Gaseous Triatomic Ions at 298.15 K

no.	ion	r_{12},[a] nm	r_{23},[a] nm	angle 123,[a] deg	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	S_i°(g), J K^{-1} mol^{-1}
13	N_3^-	0.115	0.115	180	1267	627, 636	2121	212.2
14	S_3^{2-}	0.2076	0.2076	114.9	458	227, 238	476	285.4
15	Br_3^-	0.253	0.254	171	164	52	191	326.5
16	I_3^-	0.293	0.293	180	114	53	145	334.7
17	HF_2^-	0.1136	0.1136	180	1217	952	1364	211.3
18	HOO^-	0.0931	0.1340	96.6	~3000	900-1100	~1200	228.6
19	BO_2^-			see text				215.8
20	AlO_2^-	0.161	0.161	180	690	400	1020	229.5
21	NO_2^+	0.110	0.110	180	1396	598	2360	214.1
22	NO_2^-	0.1236	0.1236	115.4	1238	826	1322	236.3
23	ClO_2^-	0.157	0.157	106	790	400	840	257.0
24	VO_2^+	0.166	0.168	105	875	558	1024	259.0
25	UO_2^{2+}	0.1774	0.1774	180	869	177	931	260.4
26	UO_2^+	0.182	0.182	180	802	160-210	885	269[b]
27	NCO^-	0.127	0.113	180	1241	630	2155	218.9
28	NCS^-	0.117	0.161	180	735	480	2059	232.5
29	$AgCl_2^-$	0.254	0.254	180	268	88	333	290.7
30	$AgBr_2^-$	0.272	0.272	180	170	61	253	315.1
31	AgI_2^-	0.285	0.285	111 180	133	49	215	349.8 330.4

[a] In XY_2 ions, X is atom number 2; in XYZ ions, X is number 1, Y number 2, and Z number 3. [b] This includes R ln 2 from the spin multiplicity.

203 J K^{-1} mol^{-1}, without specifying his input data.

5. **Peroxide, O_2^{2-}.** The value of r is from Abraham (1954),[12] and has an uncertainty of 0.004 nm, the value of ν is from Blunt (1969)[13] and any reasonable uncertainty in it is immaterial. The uncertainty of S_i°(g) is thus ±0.4 J K^{-1} mol^{-1}. It is not clear how Altschuler arrives at the lower value S_i°(g) = 194 J K^{-1} mol^{-1} on the basis of the data from ref 12. Krestov[7] gives the estimate 197 J K^{-1} mol^{-1}, which is nearer the present value. The JANAF 1982 supplement[14] lists the much higher value 209.5 J K^{-1} mol^{-1}.

6. **Hypochlorite, ClO^-.** The values of r and ν are from Heaton (1968)[15] and Kujumzelis (1938),[16] respectively. The former is from theoretical calculations, and equals the interatomic distance in the neutral chlorine monoxide, instead of being larger, as expected.[17] The observed frequency for ClO^- however, is smaller than that of ClO, in conformance with the expectation.

7. **Hypobromite, BrO^-.** The value of r is from ref 10, pertaining to the neutral molecule. It is expected that in the anion r would be somewhat larger. An increase in r of up to 0.005 nm, which is the maximal expected, would raise S_{rot} by 0.5 J K^{-1} mol^{-1}. The value of ν is from Sombret (1975),[18] and is deemed not to limit the accuracy of S_i°(g). No previous value of this quantity has been published.

8. **Nitrosonium, NO^+.** The values of r and ν are from ref 10, the uncertainties in either leading to an uncertainty of S_i°(g) of <0.1 J K_-^1 mol^{-1}. Altschuler[5] gives an estimate of 193 J K^{-1} mol^{-1}, based on an uncertain value of r, whereas Krestov[7] gives an estimate of 199 J K^{-1} mol^{-1}, which is near the present value.

9. **Vanadyl(IV), VO^{2+}.** The values of r from Palma-Vitorelli (1956)[19] and of ν from Evans (1963)[20] have small uncertainties, leading to an uncertainty in S_i°(g) <0.1 J K^{-1} mol^{-1}. No previous value for S_i°(g) has been reported.

10. **Cyanide, CN^-.** The values of r and ν are from ref 10 and have small uncertainties (for r) or such (for ν) that lead to an immaterial uncertainty in S_i°(g). Altschuler[5] gives a value based on a rather uncertain (±0.005 nm) low value of r, 189 J K^{-1} mol^{-1}, and Vasilev et al.[6] give a similar value, 188 J K^{-1} mol^{-1}. Krestov[7] gives a value, 195 J K^{-1} mol^{-1}, nearer the present value.

11. **Disulfide, S_2^{2-}.** The values of r from Föppl (1962)[21] and of ν from Janz (1976)[22] have uncertainties that contribute ±0.2 and ±0.1 J K^{-1} mol^{-1}, respectively, to S_i°(g). No value of S_i°(g) has previously been reported.

12. **Dimercury(I), Hg_2^{2+}.** The values of r from Gager (1966)[23] and of ν from Quicksall (1970)[24] pertain to the aqueous ion. The distance in a solid mercury(I) complex and the corresponding vibration frequency may differ.[25] If the latter values are taken, S_i°(g) is lowered by 2.0 J K^{-1} mol^{-1}. No value of S_i°(g) has previously been published.

B. Triatomic Ions

The data for the triatomic ions, for most of which $\bar{S}_i^{\infty}$(aq) data are available, are collected in Table II. Values of S_i°(g) for many of these ions have been published previously, but for others, namely: S_3^{2-}, Br_3^-, I_3^-, HO_2^-, VO_2^+, $AgCl_2^-$, $AgBr_2^-$, and AgI_2^-, values are given here for the first time. For the former group the values have been recalculated with updated structural and vibrational frequency data. Following are comments on these values, the sources of the input data, and a comparison with previously published values.

13. **Azide, N_3^-.** The ion is linear and symmetrical, and the interatomic distances $r_{12} = r_{23}$, and the vibrational frequencies are from Fadini (1980).[26] Uncertainties of 0.001 nm in the distance and 10 cm^{-1} in the bending mode frequency (ν_2) cause uncertainties of 0.1 J K^{-1} mol^{-1} each in S_i°(g). The value published by Altschuler[5] agrees well with the present value, that given by Krestov[7] is considerably higher.

14. **Trisulfide, S_3^{2-}.** The ion is bent, and its structure and vibrational frequencies concern BaS_3, but they are confirmed by data for K_2S_3.[27] An uncertainty of 10 cm^{-1} at the frequency of ν_2 causes an error of ±0.3 J K^{-1} mol^{-1} in S_i°(g). The precision of the structural data is sufficient to render errors due to them negligible. No value of S_i°(g) has been reported previously.

15. **Tribromide, Br_3^-.** This ion seems to be slightly nonlinear and slightly nonsymmetric in a solid com-

pound,[28] but linear and symmetric in a solution in dichloromethane.[29] If the mean distance and a linear ion (with a degenerate bending mode) are assumed, the value of $S_i^\circ(g)$ = 317.2 J K^{-1} mol^{-1} is obtained instead of that in Table II. The vibration frequencies are from Gabes (1972).[29] No value of $S_i^\circ(g)$ has been published previously for this anion.

16. Triiodide, I_3^-. This ion seems to be more or less linear (angles as small as 176° are mentioned in ref 28) but both a symmetrical configuration[29,30] or an unsymmetrical one[28] are possible. If the nonsymmetrical configuration present in CsI_3 is taken as a basis, with r_{12} = 0.283 and r_{23} = 0.303 nm (and angle α (I–I–I) = 176°), then $S_i^\circ(g)$ = 340.1 J K^{-1} mol^{-1} is obtained. Since the frequencies correspond to a species in solution (in dichloromethane[29]), which is presumed to be symmetrical, and since no reason for asymmetry in the gaseous species is apparent, the value in Table II, based on a symmetrical configuration, is preferred.

17. Hydrogen Difluoride, HF_2^-. This ion is linear symmetric in compounds such as $NaHF_2$, KHF_2, or NH_4HF_2, and is nonsymmetric only in very special environments.[31] Only two frequencies, ν_2 and ν_3 are available from Ault (1978).[32] The symmetric stretching frequency ν_1 given in Table II has been estimated in the present work from the force constant obtained from ν_3. The values of $S_i^\circ(g)$ given by Altschuler[5] and Krestov[7] are somewhat lower and higher, respectively, being based on older interatomic distance data, and a linear configuration.

18. Hydroperoxide, HO_2^-. No structural data for this ion are available from experiment, so that a structure based on ab initio SCF calculations of Heaton (1978)[15] must be used. The only experimental vibrational frequencies known are the Raman lines at ~860 cm^{-1} (for $LiOOH{\cdot}H_2O$) at at ~830 and ~870 cm^{-1} (for $NaOOH{\cdot}H_2O$), attributed by Eysel (1975)[33] to the solid monohydrates of alkali metal hydroperoxides. From the vibrational frequencies for the radical HO_2, ν_1 = 3414, ν_2 = 1101, and ν_3 = 1385 cm^{-1}, given by JANAF[14] may be estimated those of the anion HO_2^- by using the analogous pairs ClO_2 and ClO_2^- and NO_2 and NO_2^-. The range of values thus obtained for the frequencies of HO_2^- have ν_2 ~1000 cm^{-1} as their lowest member, differing from the observed frequencies mentioned above. However, even with the minimal frequency ν_2 = 830, the total contribution of S_{vib} to $S_i^\circ(g)$ is only 1.0 J K^{-1} mol^{-1}, out of 228.6 J K^{-1} mol^{-1}, so that the uncertainty from this source is probably less than ±0.5 J K^{-1} mol^{-1}.

19. Metaborate, BO_2^-. This ion has recently been discussed in detail by Srivastava (1978)[34] and no further data of consequence have been published since. These data have been adopted in Table II. Previously, Yatsimirskii[35] has proposed the somewhat lower value, 213.8 J K^{-1} mol^{-1}, based on the isoelectronic CO_2, whereas Krestov[7] gives the value 219.7 J K^{-1} mol^{-1}, based on the "real distribution of charged species".

20. Metaaluminate, AlO_2^-. This ion, too, has been recently discussed in the JANAF supplement[36] and for lack of structural and vibrational data for this ion itself, data for the isoelectronic AlOF have been used instead[37] (see also ref 34). Krestov[7] has previously given an estimate based on the isoelectronic SiO_2, $S_i^\circ(g)$ = 227.6 J K^{-1} mol^{-1} and another, based on the "real distribution of charged species", of 233.5 J K^{-1} mol^{-1}, but with no reported input data.

21. Nitronium, NO_2^+. This ion is unstable in dilute aqueous solutions, and no value of $\bar{S}_i^\infty(aq)$ is available. It is included here since the value of the calculated $S_i^\circ(g)$ may be of use in some other context. The ion is definitely linear, although its dimensions are not so well established.[38] The frequencies for the cation of the solid tetrafluoroborate salt represent those least disturbed by the anion.[37] Previous estimates of $S_i^\circ(g)$ for this ion are 216 ± 1 J K^{-1} mol^{-1} by Altschuler[5] and 222 J K^{-1} mol^{-1} by Krestov.[7]

22. Nitrite, NO_2^-. The structure and vibrational frequencies of this anion are well established. It is bent, with dimensions and frequencies given by Fadini (1980)[26] (see also ref 38). Deviations of 2, 6, and 25 cm^{-1} in ν_2, ν_1, and ν_3, respectively (as found in previous publications, e.g., Milligan (1971)[39]), cause changes of $\ll$0.1 J K^{-1} mol^{-1} in $S_i^\circ(g)$, and are, therefore, immaterial. Previous reports of $S_i^\circ(g)$ by Altschuler[5] and Krestov[7] are practically the same as the present value.

23. Chlorite, ClO_2^-. The structure of this ion is not well established. It is known to be bent, with an angle somewhat smaller[17] than in the neutral ClO_2 (110°, see Clark (1970)[40]), and is estimated by Tanguy (1967)[41] to be 106°. The Cl–O interatomic distance in ClO_2^- has been estimated to be larger[17] than in ClO_2 (0.147 nm), and is taken to be 0.157 nm. An error of ±0.005 nm in this quantity will cause S_{rot} to change by ±0.8 J K^{-1} mol^{-1}. The vibration frequencies are from Tanguy (1967)[41] and appear to be sufficiently well established. A decrease of 4 cm^{-1} in ν_2 in solution[42] relative to the solid salt[41] causes an increase of 0.1 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty in $S_i^\circ(g)$ is, therefore, ±0.8 J K^{-1} mol^{-1}. A value of $S_i^\circ(g)$ = 254.8 J K^{-1} mol^{-1} has been published by Altschuler,[4] based on the data of Mathieu.[42]

23a. Bromite, BrO_2^-. The bromite anion is not very well characterized structurally, and in aqueous solution it readily disproportionates. Contamination by bromate of the salts and their virbational spectra cannot be excluded. The distance r(Br–O) = 0.1825 nm and the angle O–Br–O = 108.2° are for solid $LiBrO_2{\cdot}H_2O$ from LeBihan (1975).[42a] The vibration frequencies are from the Raman spectrum of an aqueous solution, given by Sombret (1973).[18] An alternative set of frequencies, obtained by Tanguy (1967)[41] from the infrared spectrum of solid $Ba(BrO_2)_2$, ν_1 = 775, ν_2 = 400, and ν_3 = 800 cm^{-1} is deemed less reliable. It leads to S_{vib} smaller by 2.2 J K^{-1} mol^{-1}. The Br–O distance given here is much larger than in BrO^- or BrO_3^- and is suspected to be in error. Hence the value of $S_i^\circ(g)$ = 269 J K^{-1} mol^{-1} is possibly 2–3 J K^{-1} mol^{-1} too large. No value of $S_i^\circ(g)$ for this ion has previously been published.

24. Dioxovanadium(V), VO_2^+. The existence of this ion in acidified solutions of vanadates(V) has been described by several authors, e.g., Bartecki (1971),[43] but has not been established beyond doubt. The same may be argued about the existence of VO_2^+ in solid compounds. Two short V–O distances in $KVO_3{\cdot}H_2O$[44] have been taken by LaSalle (1955)[45] as evidence for VO_2^+, but not unequivocally. The most positive evidence comes from the infrared spectral study of VO_2F and VO_2SbF_6, where VO_2^+ with C_{2v} symmetry seems to have been definitely established as a discrete group.[46] The structure reported in Table II, of so-called *cis*-VO_2^+, is taken from Christ (1954)[44] and the vibration frequencies from Weidlein (1966).[46] No previous value of $S_i^\circ(g)$ for this cation has been published.

25. Dioxouranium(VI) (Uranyl), UO_2^{2+}. The bond distance U–O in this ion is very sensitive to the environment, but in a seemingly nonsystematic manner (see ref 47). Most akin to the structure of the ion in water would be that in $UO_2(NO_3)_2{\cdot}6H_2O$, with six oxygen atoms in the equatorial plane perpendicular to the O–U–O axis. In this compound U–O distances of 0.1770 and 0.1749 nm and an angle α(O–U–O) of 179.1° have been found by the precise neutron diffraction work of Taylor (1963).[48] The mean values of the distance and the linear arrangement taken in Table II produce a negligible difference of S_{rot}. The vibration frequencies ν_1 and ν_2 have been taken from Toth (1981),[49] a work pertaining to an aqueous solution of unhydrolyzed UO_2^{2+} species, but for ν_3 an older value[50] has to be used. The latter differs somewhat from values in solid salts (e.g., 950–960 cm^{-1} in $UO_2Cl_2{\cdot}3H_2O$[51]) but these differences are unimportant, as long as the low frequency ν_2 is well established (see also ref 47). A value of $S_i^\circ(g)$ = 260 ± 2 J K^{-1} mol^{-1} has previously been estimated by one of the authors (Marcus (1975)[52]), on the basis of reports by Krestov[7] and by Altschuler[5] for UO_2^+ (see below).

25a. Dioxoneptunium(VI), -plutonium(VI), and -americium(VI), NpO_2^{2+}, PuO_2^{2+}, and AmO_2^{2+}, Respectively. Incomplete data are available for the valuation of $S_i^\circ(g)$ for these linear ions. In particular the doubly degenerate bending mode frequencies ν_2 are not known. A set of consistent values of $r_{12} = r_{23}$ for UO_2^{2+}, NpO_2^{2+}, and PuO_2^{2+}, 0.178, 0.180, and 0.182 nm, is available from Volkov (1976),[53] and may be extrapolated to 0.183 nm for AmO_2^{2+}. Values of the Raman-active ν_1 are available from Basile (1974):[54] 872, 863, 835, and 796 cm^{-1} for UO_2^{2+}, NpO_2^{2+}, PuO_2^{2+}, and AmO_2^{2+}, respectively. Corresponding infrared-active ν_3 values are from Vdovenko (1974):[55] 932, 934, 930, and 914 cm^{-1}, respectively. Approximate values of ν_2 can be estimated if they are assumed to be proportional to the ν_1 values, with the proportionality factor taken from the known values of UO_2^{2+}. The free ions have 1, 2, and 3 unpaired electrons in the 5f orbitals of the hexavalent Np, Pu, and Am atoms, respectively. The resulting values of $S_i^\circ(g)$ {Marcus (1983)[56]} are 266, 270, and 274 J K^{-1} mol^{-1}, with uncertainties of ±2 J K^{-1} mol^{-1}.

26. Dioxouranium(V), UO_2^+. This ion is very unstable in aqueous solutions and disproportionates readily. Neither is it present as an easily identified group in solid compounds. Its structure seems to be linear, and the bond length U–O can be estimated from the increase observed from the value in MO_2^{2+} to the value in MO_2^+ of 0.005 ± 0.001 nm for M = Np and Am.[50] The uncertainty in the bond length of even 0.002 nm involves an uncertainty in $S_i^\circ(g)$ of only 0.2 J K^{-1} mol^{-1}. The vibration frequencies ν_1 and ν_3 are from Green (1973),[57] but no value has been found for ν_2. The latter can be estimated from the effect of the charge on similar species: a decrease by ~10% or an increase of ~20% have been noted, per unit change in charge. On the basis of ν_2 = 177 cm^{-1} in UO_2^{2+}, values between 160 and 210 cm^{-1} are therefore expected in UO_2^+. The uncertainty produced in S_{vib} is ±2.1 J K^{-1} mol^{-1}. The spin multiplicity of the odd electron in UO_2^+ produces a contribution of R ln 2 to the entropy. The total uncertainty of $S_i^\circ(g)$ is therefore about ±2 J K^{-1} mol^{-1}. Previous estimates of 257 ± 2 J K^{-1} mol^{-1} by Altschuler[5] and 263 J K^{-1} mol^{-1} by Krestov[7] are seen to be too low. The former value[5] is based on data for UO_2^{2+} presented in ref 50, and it is unclear why they have been assigned to UO_2^+. No source of the data is given for the value presented by Krestov,[7] and it is suspected, again, that UO_2^{2+} is meant. Since no reliable value of S_i^∞(aq) is available for the very unstable ion UO_2^+(aq), the inclusion of this ion in the present paper is, thus, only to show the difference between its $S_i^\circ(g)$ and that assigned to it previously by mistake, and which belongs more properly to UO_2^{2+}.

26a. Dioxoneptunium(V), -plutonium(V), and -americium(V), NpO_2^+, PuO_2^+, and AmO_2^+, Respectively. The linear pentavalent dioxoneptunium and -americium ions are considerably more stable than that of uranium, but that of plutonium disproportionates readily. The information required for the calculation of $S_i^\circ(g)$ is, however, incomplete for all these ions; even for NpO_2^+ the bending mode frequency ν_2 is not known. The value $r_{12} = r_{23}$ = 0.1834 nm has been found by Lychev (1980)[58] for the Np–O bond in $Cs_2NpO_2(CH_3CO_2)_3$. The values for PuO_2^+ and AmO_2^+ are unknown, and are estimated to be 0.185 and 0186 nm, respectively. Values of ν_1 = 767 cm^{-1} for NpO_2^+ and 730 cm^{-1} for AmO_2^+ are given by Basile (1974),[54] the value 750 cm^{-1} for PuO_2^+ may be estimated by interpolation. The values of ν_3 = 787 cm^{-1} for NpO_2^+, 792 cm^{-1} for PuO_2^+, and 788 cm^{-1} for AmO_2^+ are from Vodovatov (1976).[59] Values of ν_2 are estimated on the same basis as for the corresponding hexavalent actinides, see above. There should be 2, 3, and 4 unpaired electrons in the 5f orbitals of the pentavalent atoms of Np, Pu, and Am, respectively. The resulting values of $S_i^\circ(g)$ {Marcus (1983)[56]} are 272, 275, and 278 J K^{-1} mol^{-1}, with an estimated uncertainty of ±3 J K^{-1} mol^{-1}.

27. Cyanate, NCO^-. No adequate recent structural data have been found for this ion, so that the old data that have already served Altschuler[5] must be used. More recent vibrational spectral data are available from Ellestad (1972)[60] and Ti (1976).[61] The uncertainty in ν_2 (due to discrepancies between the Raman and infrared data and the nondegenerate frequencies of this linear ion in a crystalline solid) of ±7 cm^{-1} produces an uncertainty of <0.1 J K^{-1} mol^{-1} in S_{vib}. Previous reports of $S_i^\circ(g)$ are 221.8 J K^{-1} mol^{-1} by Altschuler[5] and 227.6 J K^{-1} mol^{-1} by Krestov,[7] both higher than the present value, estimated to have an uncertainty of ±1.0 J K^{-1} mol^{-1}.

28. Thiocyanate, NCS^-. Also for this ion no adequate recent structural data have been found, and the older data of Jones (1956)[62] are again used. The use of an alternative set of distances[63] changes S_{rot} only by 0.3 J K^{-1} mol^{-1}. Various, slightly different, sets of vibration frequencies are available, the one used here is from Irish (1979).[64] The total variability of S_{vib} due to these differences in the frequencies is 0.4 J K^{-1} mol^{-1}. The total error in $S_i^\circ(g)$ is therefore estimated at ±0.3 J K^{-1} mol^{-1} from all these sources. Previous reports of this value are 232.2 J K^{-1} mol^{-1} by Altschuler, in good agreement with the present value, and 238.1 by Krestov,[7] which is definitely too high.

TABLE III. Standard Molar Entropies of Gaseous Tetraatomic Ions at 298.15 K

no.	ion	r, nm	α, deg	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}	S_i°(g), J K^{-1} mol^{-1}
32	OH_3^+	0.098	107.4	3560	1095	3510	1600	192.8
33	ClO_3^-	0.1477	107.1	433	608	977	477	264.3
34	BrO_3^-	0.1648	104.1	805	418	805	358	278.7
35	IO_3^-	0.1802	104.5	805	358	775	320	288.2
36	SO_3^{2-}	0.1526	105.4	966	473	933	620	264.3
37	SeO_3^{2-}	0.1705	100.9	810	425	740	372	284.0
38	TeO_3^{2-}	0.1867	99.3	758	364	703	326	294.5
39	NO_3^-	0.1218	120.0	1049	830	1380	719	245.2
40	CO_3^{2-}	0.129	120.0	1087	874	1432	706	246.1
41	VO_3^-	0.166	120.0	932	(564)	898	360	266.9
42	HCO_2^-	[a]		2803	1349	762[b]	1585[b]	238.2
43	*trans*-$N_2O_2^{2-}$	0.120[c]	115.	1350	1120	697[d]	485[d]	256.9
	cis-$N_2O_2^{2-}$			830	1314	584[d]	1047[d]	268.4

[a] r(C-H) = 0.106 nm, r(C-O) = 0.125 nm, α(O-C-O) = 127°. [b] ν_3 and ν_4 are not degenerate, ν_5 = 1380 cm^{-1}, and ν_6 = 1066 cm^{-1}. [c] r(N-O) = 0.136 nm. [d] ν_3 and ν_4 are not degenerate, for the trans form ν_5 = 1015, ν_6 = 368 cm^{-1}, for the cis form ν_5 = 330, ν_6 = 350 cm^{-1}.

29. Dichloroargentate(I), $AgCl_2^-$. Although the dihaloargentate(I) anions are labile in aqueous solutions, a value of $\bar{S}_i^\infty$(aq) has been assigned to $AgCl_2^-$ in ref 2, hence these ions are included in this paper. The frequencies of the dihaloargentate ions have been measured by Waters (1971)[65] in solutions in tri-*n*-butyl phosphate, containing an excess of lithium halide. The mutual exclusion of the Raman- and infrared-active lines indicates that the ion is linear. No structural data on $AgCl_2^-$ in solution are available, and in a solid, the Ag–Cl distance is for a tetrahedral arrangement, rather than for a linear one.[66] For lack of a better one, this distance has been adopted here. No previous value of S_i°(g) for this ion has been proposed.

30. Dibromoargentate(I), $AgBr_2^-$. See the comments on dichloroargentate. Structural data are available for solid complexes, such as $Ni(H_2NC_2H_4NH_2)_3^{2+}(AgBr_2^-)_2$,[67] and $Au\{S_2CN(C_4H_9)_2\}_2^+$-$AgBr_2^-$, where $AgBr_2^-$ is linear.[68] The frequencies pertain to a solution in tri-*n*-butyl phosphate.[65] No value of S_i°(g) has been published previously.

31. Diiodoargentate(I), AgI_2^-. Although the vibrational spectral data indicate a linear species in tri-*n*-butyl phosphate solution,[65] a structural study in a solvent of similar donor properties, namely acetone, indicates a bent structure.[69] The Ag–I distance found in the latter study agrees with that found in solid compounds, e.g., the tris(ethylenediamine)nickel compound mentioned above.[67] Since there are no further data on which a decision between these two configurations can be made, both sets (i.e., the linear and the bent forms) have been used for the calculations. The difference in S_i°(g) of about 20 J K^{-1} mol^{-1} is so large because going from a linear to a bent configuration involves the replacement of a vibrational degree of freedom with a rotational one. Such a large difference is found also for bent forms of $AgCl_2^-$ and $AgBr_2^-$, if these are preferred. The ultimate aim is a comparison with aqueous solutions, but no structural data are available for the aqueous AgX_2^- species, which have been recognized as being formed among others. No value of S_i°(g) has so far been published for AgI_2^-.

C. Tetraatomic Ions

Most of the tetraatomic ions for which values of $\bar{S}_i^\infty$(aq) are available, and therefore are included in this study, are of the XY_3 type and have trigonal symmetry. Some are planar, such as NO_3^- and CO_3^{2-}, and others are pyramidal. They are characterized, therefore, by one interatomic distance r(X–Y), and one angle (Y–X–Y). They have four fundamental vibration frequencies, of which ν_3 and ν_4 are doubly degenerate. The input data and the resulting S_i°(g) are shown in Table IV. The S_i°(g) values of several of the ions listed have not been reported before: these include OH_3^+, IO_3^-, VO_3^-, and the two ions without trigonal symmetry, HCO_2^- and $N_2O_2^{2-}$.

32. Oxonium (Hydronium), OH_3^+. The O–H distance in the oxonium ion is not much different from that in the hydroxide ion (see Table I). The H–H distance given by Kakiuchi (1951)[70] leads to the value of α in Table III. The value of S_{rot} is not very sensitive to this value. The vibrational frequencies are those observed by Huong (1974)[71] in a solution of oxonium hexachloroantimonate, but the frequencies are sufficiently high to contribute only negligibly to the entropy (only 0.3 J K^{-1} mol^{-1} altogether). No value of S_i°(g) for this ion has been reported previously.

33. Chlorate, ClO_3^-. The reported values of r vary from 0.1477 nm,[72] given in Table III, to 0.1502 nm[73] and the reported values of the angle α deviate from the value chosen in Table III by 0.7° at most. These variations are responsible for an uncertainty of 0.7 J K^{-1} mol^{-1} in S_{rot}. The vibration frequencies are from Gardner (1972),[72] valid for aqueous solutions. There is no alternative set to be considered. The vibrational contributions do not add significantly to the overall uncertainty in S_i°(g) of ±0.4 J K^{-1} mol^{-1}. Previously reported values are 266.9 J K^{-1} mol^{-1} by both Altschuler[4] and Krestov.[7]

34. Bromate, BrO_3^-. The value of r presented in Table III from Abrahams (1977)[74] is more precise than that previously reported in ref 72. The angle α differs too, by 4.6°. The resulting net difference in S_{rot} is only 0.4 J K^{-1} mol^{-1}, however. The vibration frequencies of Gardner (1972),[72] valid for aqueous solutions, have been preferred to those obtained by Kondilenko (1976)[75] for solid $NaBrO_3$, and the uncertainty in S_{vib} due to the different sets of frequencies amounts to 1.4 J K^{-1} mol^{-1}. No value of S_i°(g) has previously been published.

35. Iodate, IO_3^-. The values of r and α from Gardner (1972)[72] together with the vibrational frequencies from the same source serve for the present calculations. Values of r differing by up to 0.0007 nm cause no appreciable difference in S_{rot}. No significantly different alternative set of vibration frequencies need be considered. No value of $S_i°(g)$ for this ion has previously been reported.

36. Sulfite, SO_3^{2-}. The values of r and α recently published by Archer (1979)[76] have been used for the calculation, previous values being less precise. The vibration frequencies, pertaining to aqueous solutions, are from Brown (1972).[77] Alternative values of α (up to 112°) change S_{rot} by 0.2 J K^{-1} mol^{-1}, alternative values of the frequencies[78] change S_{vib} by 0.8 J K^{-1} mol^{-1}, so that the total uncertainty of $S_i°(g)$ is ±0.4 J K^{-1} mol^{-1}. Previous reported values of $S_i°(g)$ are 265.3 J K^{-1} mol^{-1} by Altschuler[4] and Vasilev et al.[6] and 262.8 J K^{-1} mol^{-1} by Krestov.[7]

37. Selenite, SeO_3^{2-}. The structural data of Wagner (1975)[79] for a representative compound, $MnSeO_3 \cdot 2H_2O$, have been used, see Table III. The uncertainty in r is ±0.0011 nm, and causes an uncertainty of ±0.1 J K^{-1} mol^{-1} in S_{rot}. Vibrational frequencies for an aqueous solution are from Walrafen (1960).[80] These frequencies are essentially the same as those given by Siebert (1955)[81] for solid Na_2SeO_3, the differences correspond to 0.1 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty in $S_i°(g)$, thus, does not exceed ±0.2 J K^{-1} mol^{-1}. No previous value of $S_i°(g)$ has been published.

38. Tellurite, TeO_3^{2-}. The structure of this ion is similar to that of SO_3^{2-} and SeO_3^{2-}, and the values of r and α in Table III are those of Folger (1975)[82] which are very similar to those of Thuemmel (1974)[83] for Rb_2TeO_3. The small difference is in the angle, and leads to a difference <0.1 J K^{-1} mol^{-1} in S_{rot}. The vibration frequencies given by Walrafen[80] are for an aqueous solution. No other set of frequencies has been found, but no large uncertainties are expected, since the frequencies shown in Table III follow the pattern expected for SO_3^{2-}, SeO_3^{2-}, and TeO_3^{2-}. An uncertainty of 10 cm^{-1} in the lowest frequency, doubly degenerate ν_4, leads to an uncertainty of 0.4 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty estimated for $S_i°(g)$ is ±0.3 J K^{-1} mol^{-1}. No previous value of $S_i°(g)$ has been reported.

39. Nitrate, NO_3^-. A value of r accurate to ±0.0004 nm from Sass (1956)[84] pertains to $NaNO_3$. The ion is planar, hence α is exactly 120°. The set of vibration frequencies from Irish (1981)[85] pertains to aqueous solutions; a range of slightly different values is given in ref 78. The uncertainties in r and the different frequencies cause a maximal uncertainty of ±0.3 J K^{-1} mol^{-1} in $S_i°(g)$. Previously reported values of Altschuler,[4] Vasilev et al.,[6] and Krestov[7] are 246.0, 243.9, and 245.3 J K^{-1} mol^{-1}, respectively.

40. Carbonate, CO_3^{2-}. The value of r in the carbonate anion depends strongly on the counter cation in the solid salt,[86] and ranges from 0.129 nm to 0.132 nm, the ion being planar and the angle α being exactly 120°. The uncertainty in the bond length causes an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{rot}. The vibration frequencies are from ref 76, but a somewhat different set[72] does not change S_{vib} to a significant extent. The total uncertainty in $S_i°(g)$ is ±0.3 J K^{-1} mol^{-1}. The values reported previously for this ion are by Altschuler,[4] Vasilev et al.,[6] and Krestov,[7] being 246.0, 245.6, and 245.6 J K^{-1} mol^{-1}, respectively.

41. Metavanadate, VO_3^-. This ion does not exist as an isolated species either in solids (a salt such as NH_4VO_3 or $NaVO_3$ consists of an infinite chain of vertex-sharing VO_4 tetrahedra) or in solution (where it seems to exist as a cyclic trimer or tetramer, again consisting of vertex-sharing VO_4 tetrahedra). Still, a value of $S_i^{\infty}(aq)$ has been reported[2] for this ion, as if it existed in this form at infinite dilution in an aqueous solution. Since no structural or vibrational data for discrete VO_3^- units have been published, it is necessary to estimate them from analogous species. The VO_3^- ion is isoelectronic with TiO_3^{2-} and CrO_3, but these two moieties are themselves polymeric, the latter even in the vapor phase.[88] The VO_3^- ion should be planar like the NO_3^- ion with similarly hybridized orbitals. The distance V–O is nearer the 0.166 nm of the terminal V–O in the VO_4 tetrahedron than the 0.180 nm in a bridging V–O–V bond.[89] The symmetric and asymmetric stretching frequencies ν_1 and ν_2 should be similar to those in VO_4 tetrahedra,[89,90] as should be the O–V–O deformation frequency ν_4. The out-of-plane vibration ν_2, however, is diffucult to estimate. In a matrix-isolated WO_3, assumed to be a planar monomeric molecule of symmetry D_{3h},[91] the value assigned to this frequency is 564 cm^{-1}. This is a lower limit for the corresponding frequency in VO_3^-. The value of S_{vib} has been calculated on this basis.

42. Formate, HCO_2^-. This ion is planar, and its moment of inertia has been reported directly by Spinner (1975),[92] in rough agreement with the value calculated from the dimensions given by Müller (1967)[93] shown in the footnote of Table III. The vibration frequencies are nondegenerate and the two sets available from Müller (1967)[93] and Ito (1956)[94] produce essentially the same S_{vib}. The uncertainty in $S_2°(g)$ is thus very small, perhaps ±0.2 J K^{-1} mol^{-1}. No value of $S_i°(g)$ for this ion has been reported previously.

43. Hyponitrite, $N_2O_2^{2-}$. This ion seems to exist in two forms, *cis*- and *trans*-O—N=N—O^{2-}, with r_1 the N–N distance and r_2 the N–O distance, and the N–N–O angle = 115° from Rauch (1961).[95] For the trans form, several sets of frequencies have been reported, complete ones by McGraw (1967)[96] and Goldbloom (1976),[97] which are in agreement concerning the assignments, and that of Ranch (1966),[98] adopted by Nakamoto (1977),[116] which differs in the assignments of ν_4 and ν_6. For the cis form an incomplete set of vibration frequencies is available from Goubeau (1963),[99] and the out-of-plane deformation ν_6 is estimated here to be in the range 350–500 cm^{-1}, enclosing the extreme values given for the corresponding vibration of the trans form. The uncertainty in S_{rot}, due to estimated uncertainties of ±0.001 nm in r_1 and r_2 and of 3° in the N–N–O angle, leads to an uncertainty in $S_i°(g)$ of ±0.2 J K^{-1} mol^{-1} for both forms. The uncertainty in S_{vib} is ±1.1 J K^{-1} mol^{-1} for the cis form (due to the uncertainty in ν_6, mainly) and ±0.1 J K^{-1} mol^{-1} for the trans form. The difference in $S_i°(g)$ between the two forms amounts to 14.5 J K^{-1} mol^{-1}.

D. Pentaatomic Ions

Among the pentaatomic ions there is a large class of highly symmetrical ions, the regular-tetrahedral MO_4^{n-} anions of oxy acids. These will be discussed first, whereas other regular tetrahedral ions (such as NH_4^+ and BF_4^-) or non-regular-tetrahedral ions {such as HCO_3^- or $Ag(CN)_2^-$} will be dealt with further on.

TABLE IV. Standard Molar Entropies of Tetrahedral Gaseous Ions of the Type MO_4^{n-} at 298.15 K

no.	ion	r, nm	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}	S_i°(g), J K^{-1} mol^{-1}
44	ClO_4^-	0.146	928	459	1119	625	263.0
45	BrO_4^-	0.161	801	331	874	411	282.1
46	IO_4^-	0.1775	791	268	851	306	297.0
47	MnO_4^-	0.1629	838	355	921	429	277.8
48	$^{99}TcO_4^-$	0.1711	912	347	912	325	288.5
49	ReO_4^-	0.1721	971	332	916	332	294.1
50	SO_4^{2-}	0.149	983	450	1105	611	263.6
51	SeO_4^{2-}	0.1628	833	335	875	432	281.2
52	TeO_4^{2-}	0.1805	789	273	823	333	295.7
53	CrO_4^{2-}	0.166	846	348	884	368	281.4
54	MoO_4^{2-}	0.175	897	318	841	318	291.1
55	WO_4^{2-}	0.1803	931	324	838	324	296.6
56	MnO_4^{2-}	0.1659	812	325	820	332	291.1[a]
57	PO_4^{3-}	0.1538	938	420	1017	567	266.4
58	AsO_4^{3-}	0.1669	818	350	791	405	282.9
59	SbO_4^{3-}	(0.181)	733	263	752	309	(298.5)
60	VO_4^{3-}	0.1705	827	340	780	340	284.8

[a] Contains a contribution of 5.8 J K^{-1} mol^{-1} from the spin multiplicity of the unpaired electron.

1. MO_4^{n-}-Type Ions

The regular tetrahedral MO_4^{n-} ions are characterized by a single distance r, for the M–O bond, and by four frequencies $\nu_1(1)$, $\nu_2(2)$, $\nu_3(3)$, and $\nu_4(3)$, with the degeneracies given in parenthesis, corresponding to altogether nine normal modes. The data for r are taken from recent studies of solid compounds with minimal effects of the cations, the frequencies from studies of the ions in aqueous solutions, where available. The data and resulting S_i°(g) are shown in Table IV. For several of the ions values of S_i°(g) are given here for the first time: BrO_4^-, TcO_4^-, TeO_4^{2-}, MnO_4^{2-}, SbO_4^{3-}, and VO_4^{3-}.

44. Perchlorate, ClO_4^-. In solid hydrated perchlorates of metal cations hydrogen bonding is minimal, so that $NaClO_4 \cdot H_2O$ is a suitable solid perchlorate compound. Its value of r is known with good precision.[100] The frequencies are from Siebert (1954),[101] and an alternate set by Nyqvist and Kagel (1971)[78] does not lead to an appreciably different S_{vib}. The total error in the present value due to an ±0.001 nm uncertainty in r and to the alternative set of frequencies does not exceed ±0.2 J K^{-1} mol^{-1}. The previously reported values of S_i°(g)/(J K^{-1} mol^{-1}), 264.1 ± 1.5 by Altschuler[4] and Krestov[7] and 263.2 by Yatsimirskii[35] and Vasilev[6] are in good agreement with the present value.

45. Perbromate, BrO_4^-. The value of r reported by Brown et al. (1969)[102] from a private communication of S. Siegal, B. Tani, and E. Appleman seems to be the most precise estimate of this quantity. Their set of frequencies[102] for aqueous $RbBrO_4$ is essentially the same as reported by Appleman (1969)[103] for aqueous $HBrO_4$. The total uncertainty of S_i°(g) from the ±0.001 nm uncertainty in r and the slight differences in frequencies does not exceed ±0.2 J K^{-1} mol^{-1}. No value of S_i°(g) has previously been reported for this ion.

46. Periodate, IO_4^-. Although IO_4^- is well established as an entity in solid salts, there has been some discussion of its existence in aqueous solution since it might aquate to H_nIO^{5-n}. However, vibrational spectra showing the characteristic four frequencies with the intensity ratios expected for the tetrahedral species IO_4^- have been observed[104] in aqueous solutions. The distance I–O is from Kalman (1971),[105] the frequencies are from the compilation of Basile et al. (1973),[106] pertaining to an aqueous solution. The use of an alternative set of frequencies[104] causes a change of 0.6 J K^{-1} mol^{-1} in S_{vib}, and an alternative value of r = 0.1792 nm causes a change of 0.97 J K^{-1} mol^{-1} in S_{rot}. The estimated total uncertainty of S_i°(g) is ±0.5 J K^{-1} mol^{-1}. Previously published values of S_i°(g)/(J K^{-1} mol^{-1}) are somewhat low: 295 ± 2 by Altschuler,[4] 294 by Yatsimirskii[35] and by Vasilev et al.,[6] and 290.6 by Krestov.[7]

47. Permanganate, MnO_4^-. The value of r is from Palenik (1967),[107] given with an uncertainty of ±0.0008 nm. The set of vibration frequencies is from Hendra (1968)[108] for an aqueous solution. An alternative set from Weinstock et al. (1973)[109] produces essentially the same S_{vib}. The uncertainties in r and in the frequencies cause an uncertainty of ±0.4 J K^{-1} mol^{-1} in S_i°(g). The value of S_i°(g) of 270 J K^{-1} mol^{-1} previously reported by Yatsimirskii[35] and by Vasilev et al.,[6] is significantly lower.

48. Pertechnetate, TcO_4^-. The isotope of technetium used for the calculations of S_{tr} must be specified, in principle, since in this case no natural mixture of isotopes exists. The choice of ^{99}Tc for the calculation is rather arbitrary, but only a small uncertainty in S_{tr}, 0.13 J K^{-1} mol^{-1} per one amu in the isotopic mass is produced by this arbitrariness. No effect on S_{rot} results, however, since the Tc atom is at the center of mass of the ion. The value of r is from Krebs (1976),[110] the set of frequencies from the compilation of Basile et al. (1973),[106] with an alternative set from Weinstock et al. (1967),[109] producing an S_{vib} different by 1.1 J K^{-1} mol^{-1}. The total uncertainty in S_i°(g) is estimated at ±0.6 J K^{-1} mol^{-1}. No previous value of S_i°(g) has been reported.

49. Perrhenate, ReO_4^-. The value of r is the mean of those given by Lock (1975)[111] and by Krebs (1976),[110] which differ from each other by only 0.0002 nm. The vibration frequencies are from Woodward (1956),[112] which agree well with those of Weinstock et al. (1973).[109] The total uncertainty in S_i°(g) from these sources is ±0.6 J K^{-1} mol^{-1}. Previously reported values include those of Altschuler,[4] 297 ± 3 J K^{-1} mol^{-1}, Yatsimirskii[35] and Vasilev et al.,[6] 293.7 J K^{-1} mol^{-1}, and Krestov,[7] 295.6 J K^{-1} mol^{-1}.

50. Sulfate, SO_4^{2-}. For this ion, r is the mean from an anhydrous salt, β-Li_2SO_4 from Nord (1976),[113] and of a hydrated one, $Na_2SO_4 \cdot 10H_2O$ from Levy (1978),[114] agreeing within 0.0006 nm. The values of the frequencies are from *Landoldt Börnstein*,[115] quoted by Nakamoto[116] and are from rather dated sources, but do not seem to require revision. Another commonly used set of frequencies: 451, 613, 981, and 1104 cm^{-1} also comes from a secondary source, Walrafen (1961),[117] and is seen not to differ appreciably from the former. The uncertainties in S_{rot} and S_{vib} are therefore very small indeed. The present value of S_i°(g) is therefore in accord with the previously published ones.[4-7] The estimated uncertainty of ±0.2 J K^{-1} mol^{-1} is less than that given by Altschuler,[4] ±1.2 J K^{-1} mol^{-1}, due to our lower estimate of the uncertainty of S_{vib}.

51. Selenate, SeO_4^{2-}. The value of r is from McGinnety (1972),[118] with an assigned uncertainty of 5 × 10^{-5} nm only. The values of the frequencies are from Walrafen (1963),[119] which do not differ much from those of Paetzold (1962)[120] or of Siebert (1954).[101] Previously reported values, 282 ± 3 J K^{-1} mol^{-1} by Altschuler,[4] 282.4 by Yatsimirskii,[35] or 282.3 by Vasilev et al.[6] and by Krestov[7] are in adequate agreement with the present value.

52. Tellurate, TeO_4^{2-}. As for the periodate anion, the identity of the tellurate species in aqueous solutions has been under discussion, and its formulation as TeO_4^{2-} is by no means certain, since it may aquate to give $H_nTeO_6^{6-n}$. Vibration spectra that pertain to such species in solutions of Na_2TeO_4 have been found by Erickson (1970).[121] On the other hand there are reports of four-band spectra with intensity ratios characteristic of tetrahedral species, unambiguously ascribable to TeO_4^{2-}, by Basile et al.,[106] and by Ushanova et al. (1978).[122] The first set[106] has too low values of ν_1 and ν_3, but the latter one[122] has reasonable values, as given in Table IV. The value of r has been estimated by Kalman (1971).[105] The total uncertainty in S_i°(g) is expected to be ±0.8 J K^{-1} mol^{-1}, due mainly to the discrepancy in the frequencies. No value of S_i°(g) has previously been reported.

53. Chromate, CrO_4^{2-}. The value of r is from Kalman (1971),[105] and the frequencies are from Stammreich (1958),[123] with essentially the same values given by Brawer (1977),[124] and by Weinstock et al. (1973).[109] The slight differences in the frequencies cause an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{vib}, and the overall uncertainty in S_i°(g) is ±0.4 J K^{-1} mol^{-1}. Previously reported values of S_i°(g) are all lower, 271 ± 2 J K^{-1} mol^{-1}, apparently since they are based on the lower r = 0.16 nm, which is considered to be too low.

54. Molybdate, MoO_4^{2-}. The value of r in Table IV pertains to the aqueous species of this ion, given by Johansson (1974),[125] but is within the ±0.001 nm uncertainty limits also from that in solid K_2MoO_4 given by Gatehouse (1969).[126] The frequencies are from Müller (1972),[127] alternative sets being given by Gatehouse[126] and Weinstock.[109] The differences in the frequencies are responsible for an uncertainty of ±0.8 J K^{-1} mol^{-1} in S_{vib}, those in r to an uncertainty of ±0.1 J K^{-1} mol^{-1}, so the overall uncertainty in S_i°(g) is ±0.8 J K^{-1} mol^{-1}. Previously reported values by Yatsimirskii[35] and by Vasilev et al.[6] are 292 J K^{-1} mol^{-1} and by Krestov,[7] 293.3 J K^{-1} mol^{-1}. Altschuler[4] gives a value 295 ± 2 J K^{-1} mol^{-1} for the species MoO_4^{-1}, which must have been a printing error, although it occurs twice (whereas MnO_4^- does not occur on his list, nor does MoO_4^{2-}, but the value is much too high for MnO_4^-).

55. Tungstate, WO_4^{2-}. The value of r presented in Table IV is the mean of those for Na_2WO_4 and $CaWO_4$, the difference between these two being 0.0033 nm.[128] This difference causes an uncertainty of ±0.2 J K^{-1} mol^{-1} in S_{rot}. The frequencies are from Woodward (1956),[112] with similar data given by Weinstock (1973),[109] but another set[127] has a sufficiently different ν_2 (373 cm^{-1}) to cause a difference of 1.6 J K^{-1} mol^{-1} in S_{vib}. Hence the total uncertainty in S_i°(g) is ±0.9 J K^{-1} mol^{-1}. Previously reported values are 289 J K^{-1} mol^{-1} by Yatsimirskii[35] (provided in the paper with a question mark, and not reproduced by Vasilev et al.[6]) and 288.9 J K^{-1} mol^{-1} by Krestov.[7]

56. Manganate(IV), MnO_4^{2-}. The value of r is from Palenik (1967),[129] obtained for solid K_2MnO_4. A set of vibration frequencies is given by Gonzalez-Vilchez (1972),[130] with no source quoted, but it should pertain to aqueous solutions. A similar set is given by Basile et al.,[106] the difference between these sets causing a difference of 0.3 J K^{-1} mol^{-1} in S_{vib}. The hexavalent manganese contributes an unpaired electron to this ion, which produces a contribution of R ln 2 = 5.8 J K^{-1} mol^{-1} to the entropy of the gaseous ion from its spin multiplicity. No value of S_i°(g) has been reported previously for this ion.

57. Phosphate, PO_4^{3-}. The value of r is given by Kalman[105] and also by Johansson,[125] in the latter case specifically for an aqueous solution. The frequencies are from Steger (1964).[131] The total uncertainty estimated for S_i°(g) is ±0.2 J K^{-1} mol^{-1}. Previously reported values of S_i°(g)/(J K^{-1} mol^{-1}) are 267 ± 2 by Altschuler,[4] 266 by Yatsimirskii[35] and by Vasilev et al.,[6] and 265.9 by Krestov,[7] in adequate agreement with the present value.

58. Arsenate, AsO_4^{3-}. The value of r in Table IV is from van der Veken (1977),[132] obtained for $Na_3AsO_4 \cdot 12H_2O$. The slightly different value, 0.1695 nm, by Kalman[105] causes a difference of 0.4 J K^{-1} mol^{-1} in S_{rot}. A set of frequencies for aqueous solutions given by Vansant (1973)[133] supersedes for the present purpose previous data by Siebert (1954),[101] which pertain to solid compounds. The total uncertainty estimated for S_i°(g) is ±0.3 J K^{-1} mol^{-1}. Previously reported values of S_i°(g)/(J K^{-1} mol^{-1}) are 282 ± 3 by Altschuler,[4] by Yatsimirskii,[35] and by Vasilev et al.,[6] and 282.7 by Krestov,[7] in good agreement with the present value.

59. Antimonate, SbO_4^{3-}. This ion is not very well characterized in aqueous solutions, as it is apt to aquate (to $H_nSbO_6^{7-n}$) as the periodate and tellurate ions do. A compound of the composition Na_3SbO_4 is isotypic with Na_3BiO_4,[134] and does not contain discrete SbO_4^{3-} groups. A set of four vibrations characteristic of tetrahedral species has, however, been reported for this ion by Ushanova et al.[122] If this structure is accepted, and the value of r is estimated by the method of Kalman,[105] a value of 0.181 nm is obtained. The resulting S_i°(g) is given in Table IV, with due reservation. No value of S_i°(g) for this ion has been reported elsewhere.

60. Vanadate(V), VO_4^{3-}. Orthovandates(V) are sufficiently well characterized, also in aqueous solutions, for a value of r and sets of frequencies to have been reported for the species VO_4^{3-}, the former by Kalman,[105] the latter by Basile et al.,[106] by Weinstock et al.,[109] and by Gonzalez-Vilchez.[130] The differences between these sets cause an uncertainty of 0.2 J K^{-1} mol^{-1} in S_{vib}. The

TABLE V. Standard Molar Entropies of Tetrahedral Pentaatomic Gaseous Ions (except MO_4^{n-}) at 298.15 K

no.	ion	r, nm	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}	$S_i°$(g), J K^{-1} mol^{-1}
61	NH_4^+	0.1044	3040	1680	3145	1400	186.3
62	PH_4^+	0.1382	2295	1086	2366	994	203.2
63	BH_4^-	0.1176	2275	1225	2251	1104	187.7
64	AlH_4^-	0.1512	1757	772	1676	760	207.1
65	BF_4^-	0.1389	777	360	1070	533	267.9
66	$B(OH)_4^-$	0.1428	see text				270.5
67	$Al(OH)_4^-$	0.178	see text				293.

total uncertainty in $S_i°$(g) is estimated at ±0.3 J K^{-1} mol^{-1}. No previous value of $S_i°$(g) has been reported for this ion.

60a. Silicate, SiO_4^{4-}. The compilation of Altschuler[4] includes also an entry for SiO_4^{4-}, $S_i°$(g) = 264 ± 2 J K^{-1} mol^{-1}. However, the properties attributed to this ion probably pertain to some other form of the silicate ion (perhaps to $H_2SiO_4^{2-}$) rather than to the unprotonated orthosilicate. Since no value of $\bar{S}_i^\infty$(aq) is available or likely to become available for this ion, it is not included in Table IV.

2. Other Regular-Tetrahedral Ions

Additional pentaatomic ions exist for which the standard molar entropy in the gas phase can be calculated, and in most cases compared with the corresponding $\bar{S}_i^\infty$(aq) values. These include regular-tetrahedral species: NH_4^+, PH_4^+, BH_4^-, AlH_4^-, and BF_4^-, and the "pseudo-pentaatomic" $B(OH)_4^-$ and $Al(OH)_4^-$. These are presented in Table V, with the same kind of input data (including the degeneracies of the vibration frequencies) as in Table IV. Exceptions are $B(OH)_4^-$ and $Al(OH)_4^-$, which have more than four fundamental vibrations, and are discussed further below.

Other pentaatomic ions have a miscellany of shapes: HSO_3^-, FSO_3^-, and $S_2O_3^{2-}$ are tetrahedral, but not regular. Other protonated anions are planar, HCO_3^-, and pyramidal, $HSeO_3^-$, with a hydrogen atom bonded to an oxygen atom. Finally there are the linear symmetrical $Ag(CN)_2^-$ and $Au(CN_2^-$, the planar $AuCl_4^-$ and the "pseudo-pentaatomic" planar $Pd(NH_3)_4^{2-}$ and $Pt(NH_3)_4^{2+}$. Data and results pertaining to these ions are presented in Table VI.

61. Ammonium, NH_4^+. For the purpose of comparison with the other tetrahydro ions in Table V, values of r have been taken from the same source, Krogh-Jespersen (1980)[135] (a theoretical calculation) for all four of them. The vibration frequencies are from the compilation of *Landoldt Börnstein*,[115] quoted by Nakamoto (1977),[116] but uncertainties in them are insignificant since the values are high, and their total contribution to $S_i°$(g) is only S_{vib} = 0.26 J K^{-1} mol^{-1}. An uncertainty in r of ±0.001 nm causes an uncertainty of ±0.2 J K^{-1} mol^{-1} in $S_i°$(g), which is also the estimated total uncertainty. The previously published values[5-7,35] agree with the present value within this uncertainty.

62. Phosphonium, PH_4^+. The value of r is, again, from Krogh-Jespersen (1980)[135] and the frequencies from Durig (1970),[136] obtained for solid PH_4Cl. With an experimental value of r = 0.1414 nm found for PH_4I by Schroeder (1971)[137] and frequency values obtained by Durig (1968)[138] for this salt, a value of $S_i°$(g) differing by −0.2 J K^{-1} mol^{-1} and +0.6 J K^{-1} mol^{-1} on account of S_{vib} and S_{rot}, respectively, is obtained. The total uncertainty in $S_i°$(g) is estimated at ±0.4 J K^{-1} mol^{-1}. Previously reported values are considerably higher than the present value: 210 J K^{-1} mol^{-1} by Altschuler[5] and 216 J K^{-1} mol^{-1} by Krestov[7] (where either the sign of the ion is misprinted: PH_4^- or the ion BH_4^- is meant).

63. Tetrahydroborate, BH_4^-. The B–H bond length r is from Krogh-Jespersen (1980)[135] and the frequencies are from Memon (1981),[139] obtained for $^{11}BH_4^-$ doped into RbI crystals. Other r values have been suggested, ranging from 0.116 to 0.122 nm, leading to a range of 1.3 J K^{-1} mol^{-1} in S_{rot}. On the other hand, different sets of frequencies (e.g., from Nakamoto[116]) lead to a difference of only 0.05 J K^{-1} mol^{-1} in S_{vib}, since the frequency values are high. The total estimated uncertainty in $S_i°$(g) is ±0.7 J K^{-1} mol^{-1}. Previously reported values of $S_i°$(g)/(J K^{-1} mol^{-1}) are 189 by Altschuler,[5] 186 by Yatsimirskii,[35] Vasilev et al.[6] and Krestov,[7] (using the value of the isoelectronic CH_4), and 195 by Krestov,[7] valid for the "real distribution of charged species".

64. Tetrahydroaluminate, AlH_4^-. Again, the bond length r is from Krogh-Jespersen (1980),[135] and the frequencies are from Shirk (1973).[140] The slightly different value of r = 0.1532 nm found for solid $NaAlH_4$ causes a difference of 0.3 J K^{-1} mol^{-1} in S_{rot}. The total uncertainty estimated for $S_i°$(g) is ±0.3 J K^{-1} mol^{-1}. The previously published value by Altschuler,[5] 206 ± 1 J K^{-1} mol^{-1}, is in good agreement with the present value, although based on an estimated interatomic distance. The value 212 J K^{-1} mol^{-1} given by Krestov[7] is too high, however.

65. Tetrafluoroborate, BF_4^-. The magnitude of r is from Clark (1969),[141] and is a mean, of values for alkali metal tetrafluoroborates, with a standard deviation of ±0.0002 nm. The frequencies are from Quist (1971).[142] An alternative set of Bates (1975)[143] produces essentially the same S_{vib}. The total uncertainty in $S_i°$(g) is only ±0.2 J K^{-1} mol^{-1}. The previously published value, 269 ± 1 J K^{-1} mol^{-1}, by Altschuler,[5] agrees with the present value, but the two values given by Krestov[7] 262 (for the isoelectronic CF_4) and 275 (for a "real distribution of charged species"), both in J K^{-1} mol^{-1}, differ considerably.

66. Tetrahydroxyborate, $B(OH)_4^-$. This is considered a pseudopentaatomic regular-tetrahedral ion, since for the purpose of the calculation of S_{rot} the OH group is treated as a rigid "heavy" oxygen atom, located at the position of the oxygen atom. For the purpose of the calculation of S_{vib}, however, all the 21 vibrations have, nominally, to be taken into account, although some (e.g., the O–H stretching vibration) occur at frequencies high enough not to affect the entropy. The interatomic distance r(B–O) = 0.1428 nm given by Devarajan (1974)[144] and the frequencies given there are used. The latter are from a Raman spectroscopic study and have the following values (in cm^{-1}): 499 [E_g, δ_a(BO)], 505 [B_{1g}, δ_a(BO)], 373 [B_{2g}, δ_s(BO)], 429 [A_{1g},

TABLE VI. Standard Molar Entropies of Gaseous Pentaatomic Ions, Which Are Not Regular Tetrahedra, at 298.15 K[a]

no.	ion	r_1 nm	r_2, nm	α_1, deg	α_2, deg	symmetry	$S_i°(g)$, J K^{-1} mol^{-1}
68	HSO_3^-	0.13	0.149	109.5	109.5	C_{3v}	266.8
69	FSO_3^-	0.1561	0.1426	114.7	103.5	C_{3v}	279.1
70	$ClSO_3^-$	0.199	0.144	109.5	109.5	C_{3v}	293.5
71	$S_2O_3^{2-}$	0.197	0.148	109.5	109.5	C_{3v}	291.1
72	HCO_3^-	0.143	0.125	115.5	129		257.9
73	$HSeO_3^-$	0.1764	0.1683	100	102.7		283.0
74	$Ag(CN)_2^-$	0.213	0.115	180		D_∞	280.7
75	$Au(CN)_2^-$	0.1994	0.1147	180		D_∞	284.5
76	$AuCl_4^-$	0.2288		90		D_{4h}	363.8
77	$Pd(NH_3)_4^{2+}$	0.206		90		D_{4h}	410.2
78	$Pt(NH_3)_4^{2+}$	0.217		90		D_{4h}	415.8

no.	ion	nondegenerate frequencies	doubly degenerate frequencies
68	HSO_3^-	$\nu_1 = 2530, \nu_2 = 1021, \nu_3 = 621$	$\nu_4 = 1200, \nu_5 = 1128, \nu_6 = 508$
69	FSO_3^-	$\nu_1 = 1142, \nu_2 = 842, \nu_3 = 571$	$\nu_4 = 1302, \nu_5 = 619, \nu_6 = 424$
70	$ClSO_3^-$	$\nu_1 = 1042, \nu_2 = 381, \nu_3 = 601$	$\nu_4 = 1300, \nu_5 = 553, \nu_6 = 312$
71	$S_2O_3^{2-}$	$\nu_1 = 147, \nu_2 = 670, \nu_3 = 1004$	$\nu_4 = 339, \nu_5 = 538, \nu_6 = 1106$
72	HCO_3^-	$\nu_1 = 3390, \nu_2 = 1697, \nu_3 = 1338, \nu_4 = 1211, \nu_5 = 960, \nu_6 = 712, \nu_7 = 597, \nu_8 = 835, \nu_9 = 660$	
73	$HSeO_3^-$	$\nu_1 = 615, \nu_2 = 855, \nu_3 = 410, \nu_4 = 320, \nu_5 = 790, \nu_6 = 345, \nu_7 = 2420, \nu_8 = 1235, \nu_9 = 875$	
74	$Ag(CN)_2^-$	$\nu_1 = 2146, \nu_2 = 360, \nu_3 = 2140, \nu_4 = 390$	$\nu_5 = 250, \nu_6 = 328, \nu_7 = 147$
75	$Au(CN)_2^-$	$\nu_1 = 2161, \nu_2 = 446, \nu_3 = 2141, \nu_4 = 426$	$\nu_5 = 301, \nu_6 = 411, \nu_7 = 125$
76	$AuCl_4^-$	$\nu_1 = 351, \nu_2 = 152, \nu_3 = 323, \nu_4 = 179, \nu_5 = 112$	$\nu_6 = 354, \nu_7 = 166, 177$
77	$Pd(NH_3)_4^{2+}$	$\nu_1 = 510, \nu_2 = 468, \nu_3 = 237, \nu_4 = 305, \nu_5 = 160$ (skeletal vibrations, see text)	$\nu_6 = 498, \nu_7 = 291$
78	$Pt(NH_3)_4^{2+}$	$\nu_1 = 538, \nu_2 = 526, \nu_3 = 270, \nu_4 = 234, \nu_5 = 150$ (skeletal vibrations, see text)	$\nu_6 = 510, \nu_7 = 297$

[a] The vibrational frequencies (in cm^{-1}) are given at the bottom of the Table.

δ_s(BO)], 946 [E_g, ν_a(BO)], 854 [B_{1g}, ν_a(BO)], 743 [A_{1g}, ν_s(BO)], 660 [E_g, γ(OH)], 770 [B_{2g}, γ(OH)], 1185 [E_g, δ(OH)], 1195 [A_{1g}, δ(OH)], 3535 [E_g, ν(OH)], 3525 [B_{1g}, ν(OH)], and 3555 [A_{1g}, ν(OH)]. Two further vibrations have not been observed (one being nonactive in the Raman spectrum, the other apparently of too low intensity). These are the A_{2g} γ(OH) and the B_{1g} δ(OH) vibrations, for which the values 950 and 1200 cm^{-1} are estimated in the present study. Uncertainties of ±50 cm^{-1} in each of the latter cause an uncertainty of ±0.14 J K^{-1} mol^{-1} in S_{vib}. Further uncertainties in the vibrational frequencies of the order of 2% may cause a total uncertainty of ±0.4 J K^{-1} mol^{-1} in S_{vib}. The neglect of the difference between the center of gravity of the OH "heavy atom" and the position of the oxygen atom, and uncertainties in the latter (a value of $r = 0.148$ nm has been given by Corti (1980),[145] but this seems to be too long, in view of the value of r of the isoelectronic BF_4^-) may cause an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{rot}. The total uncertainty of $S_i°(g)$ is, therefore, ±0.5 J K^{-1} mol^{-1}. A value of $S_i°(g) = 266.9$ J K^{-1} mol^{-1} has been attributed by Corti (1980)[142] to Krestov,[7] but does not appear in this reference. No other value of $S_i°(g)$ has been published.

67. Tetrahydroxyaluminate, $Al(OH)_4^-$. The value of r as well as the frequencies are from Ignatiev (1978).[146] The latter have the following values (in cm^{-1}): 312 (A_1), 328 (E), 335 (B_2), 335 (B_1), all δ(AlO); 493 (B_1), 494 (A_2), 515 (E), all γ(OH); 625 (A_1), 659 (B_2), 723 (E), all ν(AlO); 950 (E), 962 (A_1), 1005 (B_2), all δ(OH); and 3287 (A_1, B_2 and E), all ν(OH). A 2% uncertainty in the frequencies causes a total uncertainty of ±0.5 J K^{-1} mol^{-1} in S_{vib}. The Al–O distances in four-coordinated solid compounds with "isolated" AlO_4 tetrahedra vary from 0.177 to 0.180 nm, and the neglect of the coincidence of the center of gravity of the OH "heavy atom" of the pseudopentaatomic ion with the position of the oxygen atom may cause an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{rot}, so that the total uncertainty in $S_i°(g)$ is ±0.6 J K^{-1} mol^{-1}. No previous value of $S_i°(g)$ has been published.

3. *Other Pentaatomic Ions*

68. Hydrogen Sulfite, HSO_3^-. The more recent literature on this ion presents a consensus of opinions that it exists in aqueous solutions preponderantly and in solids exclusively as the ion $H–S(O)_3$, i.e., with the H atom directly bonded to the S atom, and not via an O atom {Simon (1960),[147] Hiratsue (1975),[148] Meyer (1979)[149]}. This conclusion is based on an analysis of the vibrational spectra, as no structural information from diffraction measurements is available. The value of r_1 (the S–H distance) is estimated to equal either that in HS^- (as shown in Table VI) or that in H_2S, and the value of r_2 (the S–O distance) and with it the angles α_1 (O–S–O) and α_2 (O–S–H) equal either those in SO_4^{2-} (regular tetrahedral angles, as shown in Table VI) or those in SO_3^{2-}. These four combinations produce an uncertainty of ±0.5 J K^{-1} mol^{-1} in S_{rot}. The frequencies given by Meyer (1980)[150] are listed in Table VI, since they pertain to aqueous solutions, and have been disentangled from those of $S_2O_5^{2-}$, which coexists in HSO_3^- solutions. The use of other sets of frequencies {e.g., those of Meyer (1979)[149] for the rubidium and cesium salts or of Hiratsue (1975)[148] for the ammonium salt} produce a change in S_{vib} of <0.1 J K^{-1} mol^{-1}. The total estimated uncertainty of $S_i°(g)$ is ±0.5 J K^{-1} mol^{-1}. No previous value of $S_i°(g)$ has been published.

69. Fluorosulfate, FSO_3^-. This ion is not stable in aqueous solutions but reacts slowly with water to give HF and HSO_4^-. However, it is stable in solids and in nonaqueous solvents, hence its entropy in the gaseous state is of interest. The values of r_1(F–S distance) and r_2(S–O distance) are from diffraction data on solid

$CH_3C(OH)_2^+FSO_3^-$ of Kvick (1969),[151] which are in agreement with those of O'Sullivan (1970)[152] for solid $K^+FSO_3^-$. The angles α_1 (for O–S–O) and α_2 (for O–S–F) are also from Kvick.[151] The vibration frequencies are from Alleyne (1974),[153] but alternative sets, e.g., of Josson (1977),[154] do not produce an S_{vib} different by >0.1 J K^{-1} mol^{-1}. The estimated total deviation of $S_i°(g)$ is ±0.3 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has previously been reported.

70. Chlorosulfate, $ClSO_3^-$. This ion is even less stable in aqueous solutions than FSO_3^-, but for the reasons stated above, its $S_i°(g)$ is considered to be of interest. The structure of this ion has not been studied by diffraction methods, but for the purpose of interpretation of the vibrational spectrum it has been assumed by Steger (1967)[155] to have regular-tetrahedral angles and the r_1(S–Cl distance) and r_2(S–O distance) given in Table VI. The vibrational frequencies are from Stufkens (1970),[156] obtained in a solution of $Na^+ClSO_3^-$ in dimethylacetamide. An alternative set, by Steger (1969),[157] produces a large difference (of 2.9 J K^{-1} mol^{-1}) in S_{vib} since it includes a much lower SO_3 deformation frequency (220 cm^{-1} rather than 312 cm^{-1}), which is considered less reasonable, when compared to the frequency assigned to this mode in FSO_3^-. The rough data used for the structural characteristics produce an uncertainty of ±1.0 J K^{-1} mol^{-1} in S_{rot} and with the uncertainty in S_{vib} the total uncertainty of $S_i°(g)$ is estimated at ±1.5 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been previously reported.

71. Thiosulfate, $S_2O_3^{2-}$. The values of r_1(S–S distance) and r_2(S–O distance) are from Müller (1967),[158] who has provided also the vibration frequencies. The former are in agreement with those used by Steger (1967),[155] whereas slight differences exist in the frequencies reported by the two sources. A further source, which deals explicitly with the isolated thiosulfate anion, is Gabelica (1980).[159] The total uncertainty in S_{vib} due to different input frequencies is ±0.1 J K^{-1} mol^{-1}. The range of S–S distances in thiosulfates is 0.196–0.201 nm, and this uncertainty is responsible for an uncertainty of ±0.1 J K^{-1} mol^{-1} in S_{rot}, so the total uncertainty in $S_i°(g)$ is ±0.2 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously for this ion.

72. Hydrogen Carbonate, HCO_3^-. The OH group is considered as a "heavy oxygen" atom for the purpose of the calculation of the moment of inertia. The dimensions of this ion: r_1(C–OH distance), r_2(C–O distance), α_1 (O–C–OH angle), and α_2 (O–C–O angle) are from Jonsson's theoretical calculation (1978).[160] The crystallographic data of Sharma (1965)[161] on solid $NaHCO_3$ are in essential agreement, except for the C–OH distance, which is substantially smaller, 0.1345 nm, whereas the O–H distance is larger (0.107 vs. 0.098 nm). The difference in S_{rot} caused by this is 0.5 J K^{-1} mol^{-1}. The required set of nine vibrational frequencies is from Stankevich (1978).[162] No alternative set of vibration frequencies is available, so an arbitrary uncertainty of ±2% is assigned to each, leading to an uncertainty of ±0.15 J K^{-1} mol^{-1} in S_{vib}, and to a total uncertainty of $S_i°(g)$ of ±0.3 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has previously been reported for this ion.

73. Hydrogen Selenite, $HSeO_3^-$. Contrary to the case of the hydrogen sulfite ion, the accumulated evidence points to the presence of an OH group in the hydrogen selenite ion, rather than to that of an SeH group. The structural data r_1(Se–OH distance), r_2(Se–O distance), α_1 (O–Se–OH angle), and α_2 (O–Se–O angle) are from Cody (1978).[163] An earlier set of structural data, of Chou (1963)[164] has distances larger by 1.5–3%, causing a change in S_{rot} of 0.5 J K^{-1} mol^{-1}. The vibration frequencies are from Cody (1978)[163] and Walrafen (1962),[80] with no alternative set for comparison. An arbitrarily chosen uncertainty of ±2% in each frequency produces an uncertainty of ±0.3 J K^{-1} mol^{-1}. The total uncertainty in $S_i°(g)$ is estimated at ±0.5 J K^{-1} mol^{-1}. No previous value of $S_i°(g)$ has been reported.

74. Dicyanoargentate(I), $Ag(CN)_2^-$. This ion is shown to be linear and symmetrical on the basis of the mutual exclusion of the infrared-active and Raman-active vibrational frequencies. However, the values of r_1(Ag–C distance) and r_2(C–N distance) are not known accurately, and are estimates, given by Jones (1957).[165] Several sets of vibration frequencies for this ion have been reported. Since the ion is linear, there are altogether 10 vibrational degrees of freedom, the C–Ag–C bending mode ν_7 being of twofold degeneracy. The set given by Loehr (1970),[166] pertaining to solid $KAg(CN)_2$, is presented in Table VI, and alternative sets, of Jones (1957)[165] and of Wong (1979)[167] may serve as a check. The only significant difference is in ν_7, the C–Ag–C bending mode, the values given by Loehr and Wong being in reasonable agreement, whereas the earlier value by Jones is considerably lower (107 cm^{-1}), and produces a change of 5 J K^{-1} mol^{-1} in S_{vib}. In view of the analogous value for the dicyanoaurate ion (see Table VI and below), the higher value of ν_7 is preferred. The other differences in the vibration frequencies cause a change of 0.2 J K^{-1} mol^{-1}. The fact that the value of r_1 is larger than that of dicyanoaurate, rather than being smaller, as expected, may contribute heavily (1.1 J K^{-1} mol^{-1}) to the uncertainty in S_{rot}. In view of these uncertainties, it is impossible to give a realistic estimate of the uncertainty of the calculated $S_i°(g)$. Altschuler[4] has reported $S_i°(g) = 308$ J K^{-1} mol^{-1}, based on the data of Jones,[172] but it is not clear how, from these data, such a large value could have been derived which in our calculation amounts to 285 J K^{-1} mol^{-1} only. Krestov[7] has reported an even higher value, 314 J K^{-1} mol^{-1}, without specifying the source of his data.

75. Dicyanoaurate(I), $Au(CN)_2^-$. This ion, like the previous one, is linear, and the values of r_1(Au–C distance) and r_2(C–N distance) are from the X-ray diffraction data on solid $KCo[Au(CN)_2]_3$ of Abrahams (1980).[168] The vibration frequencies are from Chadwick (1976),[169] pertaining to a solution of $K[Au(CN)_2]$ in *N*-methylpyrrolidinone. Alternative, less precise, values of the distances[170,171] are in the range from 0.198 to 0.212 nm for r_1 and from 0.110 to 0.117 nm for r_2, and lead to an uncertainty of ±0.5 J K^{-1} mol^{-1} in S_{rot}. Another set of vibration frequencies, pertaining to solid $K[Au(CN)_2]$ has $\nu_7 \approx 100$ cm^{-1}, estimated by Jones (1957),[165] and altogether leads to S_{vib} larger by 4.7 J K^{-1} mol^{-1}. The firmly established value of $\nu_7 = 125$ cm^{-1}, as well as those of the other vibrations given by Chadwick[169] for the ion in solution, are preferred, however. Since the value of ν_7 given by Jones[165] is only an estimate, it is not considered as a basis for the estimation of the uncertainty of S_{vib}. The values of $S_i°(g)$ given by Alt-

TABLE VII. Standard Molar Entropies of Gaseous Hexaatomic Ions at 298.15 K

no.	ion	r_1, nm	r_2, nm	vibration frequencies, cm^{-1}	$S_i°(g)$, $J\ K^{-1}\ mol^{-1}$
79	HSO_4^-	0.1445	0.156	$\nu_1 = 1032$, $\nu_2 = 405$, $\nu_3 = 565$, $\nu_4 = 1210$, $\nu_5 = 580$, $\nu_6 = 440$, $\nu_7 = 875$, $\nu_8 = 1160$, $\nu_9 = 2950$	283.0
80	$HSeO_4^-$	0.1625	0.176	$\nu_1 = 915$, $\nu_2 = 394$, $\nu_3 = 740$, $\nu_4 = 862$, $\nu_5 = 395$, $\nu_6 = 320$, $\nu_7 = 945$, $\nu_8 = 1000$, $\nu_9 = 2900$	295.8
81	HPO_4^{2-}	0.152	0.155	$\nu_1 = 970$, $\nu_2 = 528$, $\nu_3 = 891$, $\nu_4 = 1082$, $\nu_5 = 528$, $\nu_6 = 389$, $\nu_7 = 1230$, $\nu_8 = 2380$, $\nu_9 = 2900$	283.0
82	$H_2PO_4^-$	0.1508	0.1583	$\nu_1 = 1074$, $\nu_2 = 1082$, $\nu_3 = 893$, $\nu_4 = 878$, $\nu_5 = 1152$, $\nu_6 = 1154$, $\nu_7 = 1268$, $\nu_8 = 1224$, $\nu_9 = 949$, $\nu_{10} = 948$, $\nu_{11} = 1050$, $\nu_{12} = 820$, $\nu_{13} = 515$, $\nu_{14} = 390$, $\nu_{15} = 2360$	280.7
83	$HAsO_4^{2-}$	0.1662	0.1728	$\nu_1 = 838$, $\nu_2 = 707$, $\nu_3 = 327$, $\nu_4 = 866$, $\nu_5 = 315$, $\nu_6 = 380$, $\nu_7 = 811$, $\nu_8 = 1100$, $\nu_9 = 2800$	302.9
84	HVO_4^{2-}	0.1705	0.175	$\nu_1 = 877$, $\nu_2 = 545$, $\nu_3 = 351$, $\nu_4 = 850$, $\nu_5 = 500$, $\nu_6 = 351$, $\nu_7 = 1000$, $\nu_8 = 1200$, $\nu_9 = 2800$	296.1

schuler,[4] 308 J K^{-1} mol^{-1}, and by Krestov,[7] 313 J K^{-1} mol^{-1}, are much higher than the present value, but with no apparent reasons.

76. Tetrachloroaurate(III), $AuCl_4^-$. This ion is square planar with D_{4h} symmetry, both in aqueous solutions, as determined by Maeda (1974),[173] and in salts, such as $KAuCl_4{\cdot}2H_2O$, as determined by Theobald (1980).[174] Hence $r_1 = r_2$ is the Au–Cl distance, and all the Cl–Au–Cl angles have $\alpha_1 = \alpha_2 = 90°$. Of the nine vibrational frequencies, one, ν_5, is both Raman and infrared inactive, and is observed only as an overtone or combination line. Goggin (1974)[175] gives a full complement of seven frequencies, of which ν_6 and ν_7 are twofold degenerate, see Table VI. The various reported values of r are within 0.001 nm of each other, so the uncertainty of S_{rot} is $<\pm 0.1$ J K^{-1} mol^{-1}. Alternative sets of the frequencies are incomplete: Hendra (1967)[176] gives only ν_1, ν_3, ν_4, ν_6, and ν_7, Bosworth (1975)[177] reports only ν_1, ν_3, and ν_4, both in general agreement with the set given above in frequency values, but not necessarily in the numbering of the nondegenerate ν_3 and ν_4 modes. These lead to a difference in S_{vib} of ±0.5 J K^{-1} mol^{-1}, which is also the total uncertainty in $S_i°(g)$. No previous value of $S_i°(g)$ has been published.

77. Palladium(II) Tetraammine, $Pd(NH_3)_4^{2+}$. This ion, too, is a square-planar ion, with D_{4h} symmetry, provided free rotation of the NH_3 ligands around the Pd–N bonds is permitted. With this proviso, four vibrational degrees of freedom out of the forty five are converted into internal rotations. The Pd–N distance, r, is from Bell (1976),[178] the N–H distance is taken as 0.100 nm, for the purpose of the calculation of the free rotation contributions to the entropy. For the rotational contribution, the NH_3 groups are considered as "heavy nitrogen" atoms, located at the center of gravity of the group. The skeletal vibrational frequencies (i.e., Pd–N stretches and N–Pd–N bends) are from Schmidt (1974),[179] except for ν_5, the out-of-plane vibration, estimated at 160 cm^{-1}, according to Perry (1967).[180] The bending and rocking frequencies of the NH_3 ligands must also be taken into account: according to Manfait (1980)[181] there are three NH_3 wags at 166 cm^{-1}, seven NH_3 rocks at 811 cm^{-1}, four NH_3 bends at 1289 cm^{-1}, seven NH_2 bends at 1586 cm^{-1}, and NH stretches at >3000 cm^{-1}, that do not contribute significantly to S_{vib}.

Uncertainties arise from several sources: the Pd–N distance has been given as only 0.200 nm by Hiraishi[182] and Hendra.[183] For the skeletal vibrations Manfait[181] takes $\nu_4 = 264$ instead of the 305 cm^{-1} of Schmidt,[179] whereas Hendra[183] takes $\nu_7 = 245$ instead of the latter's 291 cm^{-1}. Alternative values for the ligand vibrations (802, 1279, and 1630 cm^{-1}) instead of those quoted above also cause uncertainties, since these frequencies are of high apparent degeneracies. Finally, the notion of the free rotation of the NH_3 groups is not fully established. The total uncertainty of $S_i°(g)$ due to all these sources is ±2.2 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

78. Platinum(II) Tetraammine, $Pt(NH_3)_4^{2+}$. This ion is similar to the palladium analogue in geometry, hence also in the treatment accorded to it. The Pt–N distance r is from Hiraishi (1968)[182] or Hendra (1967).[183] The skeletal vibrations are taken from Schmidt (1975),[179] except for the out-of-plane vibration $\nu_5 = 150$ cm^{-1}, taken from Poulet (1964).[184] The ligand vibrations are also taken from the latter authors: seven NH_3 rocks at 842 cm^{-1}, four NH_2 bends at 1325 cm^{-1} and seven NH_2 bends at 1560 cm^{-1}, whereas three NH_3 wags at 201 cm^{-1} are taken from Adams (1973).[185] The N–H stretching frequencies at >3000 cm^{-1} do not contribute significantly to S_{vib}. The free rotation of the four NH_3 groups around the Pt–N bonds contributes to S_{rot}, as for the palladium analogue.

Uncertainties arise mainly from the conflicting assignments of the vibration frequencies. Hiraishi[182] and Poulet[184] assign 235 cm^{-1} to ν_5, 150 cm^{-1} to ν_3 and 265 cm^{-1} to ν_4, respectively, and Adams[185] gives 241 cm^{-1} for ν_3 and 267 cm^{-1} for ν_4. Values of 828 and 888 cm^{-1} for the NH_3 rocking frequencies, and 1355 cm^{-1} and 1630 cm^{-1} for the NH_2 bending frequencies are given by Poulet[184] for some of the lines. The total uncertainty in S_{vib} from these sources is ±2.5 J K^{-1} mol^{-1}. Again, the notion of free rotation of the NH_3 ligands may be uncertain. No previous value of $S_i°(g)$ has been reported.

E. Hexaatomic Ions

A significant group of hexaatomic ions, which have not been dealt with in this connection in the past, are the ions of the hydrogen sulfate type, HMO_4^{n-}. These have C_{3v} symmetry, if free rotation of the hydroxy group is assumed, and as in previous cases (see HCO_3^-, for instance), the OH group is treated as a "heavy oxygen" atom for the purpose of the calculation of the rotational contribution to the entropy. Nine vibration frequencies must be specified for each ion, of which three (ν_4, ν_5, and ν_6) are doubly degenerate. These data are not fully available for all the ions considered, and some frequencies have to be estimated by analogy. The data and the results are shown in Table VII. The ion $H_2PO_4^-$ is heptaatomic, but is included here for comparison with HPO_4^{2-}, and its two OH groups are considered as "heavy oxygen" atoms. Its 15 vibrational frequencies are specified in Table VII, and the two angles required to complete the specification of its structure are given in the text. Two further hexaatomic ions, oxalate and dithionite, are discussed among the X_2Y_n-type ions further below.

79. Hydrogen Sulfate, HSO_4^-. The distances r_1(S–O) and r_2(S–OH) are means of the distances found in $RbHSO_4$ by Ashmore (1975),[186] which are representative of these distances in other salts, ranging from 0.144 to 0.147 nm for r_1 and from 0.155 to 0.161 nm for r_2, according to Sonneveld (1978).[187] The uncertainties in the distances lead to an uncertainty of ±0.6 J K^{-1} mol^{-1} in S_{rot}. The frequencies are from Mielke (1973),[188] again for a $RbHSO_4$ crystal, and are in fair agreement with the incomplete set (no ν_2 and ν_9) given by Walrafen (1962)[189] for an aqueous solution. Other sets, by Siebert (1955)[81] for a solid, Dhamelincourt (1971)[190] for an NH_4HSO_4 melt, and Goypiron (1978)[191] for liquid H_2SO_4, are again in general agreement but differ in the detailed assignments, and lead to a spread of 0.9 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty in $S_i°(g)$ is estimated at ±0.8 J K^{-1} mol^{-1}.

80. Hydrogen Selenate, $HSeO_4^-$. The distances r_1(Se–O) and r_2(Se–OH) are from Waskowska (1978),[192] and the frequencies are from Walrafen (1963),[119] obtained for an aqueous solution. Another set of frequencies, by Paetzold (1962)[120] is in substantial agreement. Both sets lack values for ν_8 and ν_9, and the values listed have been estimated in the present study by analogy with the corresponding values for HSO_4^-. The uncertainty introduced by these guesses is not higher than ±0.2 J K^{-1} mol^{-1}, but uncertainties in the assignments of the observed frequencies to degenerate or nondegenerate vibrations introduce another uncertainty of ±0.2 J K^{-1} mol^{-1} in S_{vib}. The uncertainties in the bond lengths (±0.0015 nm in r_1) and possible deviations[189] of the O–Se–O and O–Se–OH angles from the assumed regular tetrahedral ones produce an uncertainty of ±0.5 J K^{-1} mol^{-1} in S_{rot}. The total uncertainty in $S_i°(g)$ is ±0.6 J K^{-1} mol^{-1}.

80a. Hydrogen Chromate, $HCrO_4^-$. This ion is recognized[193] as existing in acidified aqueous solutions of chromates besides the dichromate ion, $Cr_2O_7^{2-}$. A value of $S_i^\infty(aq)$ has been reported[194] for it. However, no structural information nor vibrational frequencies pertaining to it are known, and it has not been reported as existing in solid salts. Therefore $S_i°(g)$ cannot be calculated for it.

81. Hydrogen Phosphate, HPO_4^{2-}. The distances r_1(P–O) and r_2(P–OH) are from Müller (1967),[158] and not very precise. Alternatively, the values reported for $H_2PO_4^-$ in Table VII, may be used but these need not necessarily be applicable to HPO_4^{2-}. The frequencies are also from Müller[158] (ν_1 and ν_6), supplemented by values for ν_7, ν_8, and ν_9 from Chapman (1964),[195] which apply to an aqueous solution of K_2HPO_4. Another complete set, for solid Na_2HPO_4, is also due to Chapman,[195] and further, incomplete sets, have been given by Preston (1979)[196] and by Hanwick (1949).[197] The uncertainties in the frequencies contribute ±1.4 J K^{-1} mol^{-1} to the uncertainty in $S_i°(g)$, those in interatomic distances another ±0.3 J K^{-1} mol^{-1}, and altogether the total uncertainty in $S_i°(g)$ is ±1.5 J K^{-1} mol^{-1}.

82. Dihydrogen Phosphate, $H_2PO_4^-$. The structure of this ion has been reported by Hayes (1977),[198] and it is not regularly tetrahedral: the distances r_1(P–O) and r_2(PO–H), together with the angles 115.4° (O–P–O) and 105.5° (HO–P–OH) give a distorted tetrahedron with a C_{2v} symmetry. Two extensive sets of vibration frequencies exist, one of Steger (1977)[199] for aqueous NaH_2PO_4, by both infrared and Raman spectroscopy (shown in Table VII), and one by Chapman (1964)[195] for solid NaH_2PO_4 by infrared spectroscopy, supplemented with Raman and infrared data for aqueous solutions. A partial frequency list has also been given by Preston.[196] These sets are in general agreement, and the low symmetry of the ion causes 15 discrete frequencies to be observed, but some have observable intensities in the infrared or Raman spectra only. These alternative sets produce an uncertainty of only ±0.2 J K^{-1} mol^{-1} in S_{vib}, since most of the frequencies are fairly high. The uncertainty in S_{rot} is estimated at ±1.0 J K^{-1} mol^{-1}, so the total uncertainty in $S_i°(g)$ does not exceed ±1.0 J K^{-1} mol^{-1}.

83. Hydrogen Arsenate, $HAsO_4^{2-}$. The distances r_1(As–O) and r_2(As–OH) are from van der Veken (1977),[132] obtained for $Na_2HAsO_4{\cdot}7H_2O$. Distances larger by 1% have been obtained[132] for $(NH_4)_2HAsO_4{\cdot}7H_2O$. The frequencies ν_1 to ν_7 are from Vansant (1973),[133] but ν_8 and ν_9 have to be estimated. Reasonable uncertainties due to this necessity amount to ±0.4 J K^{-1} mol^{-1} in S_{vib} and uncertainties in the distances add another ±0.2 J K^{-1} mol^{-1} in S_{rot}, or altogether ±0.5 J K^{-1} mol^{-1} in $S_i°(g)$.

83a. Dihydrogen Arsenate, $H_2AsO_4^-$. Structural and vibration-spectroscopic information is lacking for this ion. No value of $S_i°(g)$ can be calculated, although $\bar{S}_i^\infty(aq)$ is known.

84. Hydrogen Vanadate, HVO_4^{2-}. No structural data for this ion have been found, so r_1(V–O) is assumed to be the same as in VO_4^{3-} (see also the cases of r_1 of HPO_4^{2-} and $HAsO_4^{2-}$, Table VII, compared with PO_4^{3-} and AsO_4^{3-}, Table IV). The value of r_2 is larger than that of r_1 by 4% in HPO_4^{2-} and by 2% in $HAsO_4^{2-}$, so that an increase of r_2 over r_1 in HVO_4^{2-} of 3% is assumed. Incomplete sets of vibration frequencies are reported by Griffiths (1966)[200] and by Pinchas (1969):[201] ν_1 to ν_4 and ν_6 are in essential agreement, but values of ν_5 and ν_7, ν_8, and ν_9 have to be estimated. The uncertainty introduced by the value taken for ν_5, in analogy with HPO_4^{2-} and $HAsO_4^{2-}$, leads to an uncertainty of ±1.5 J K^{-1} mol^{-1} in S_{vib}. The uncertainties in the higher frequency values of ν_7, ν_8 and ν_9 contribute another ±0.3 J K^{-1} mol^{-1}, and together with uncertainties in the distances, the estimated total uncertainty in $S_i°(g)$ is ±1.8 J K^{-1} mol^{-1}.

84a. Dihydrogen Vanadate, $H_2VO_4^-$. The comment given above for $H_2AsO_4^-$ applies here too.

F. Ions of the Type X_2Y_n ($n \geq 4$)

There are several ions of the type X_2Y_n for which entropies in the ideal gas state can be calculated, and compared with those in the aqueous standard state. They range from the hexaatomic ions, $n = 4$, oxalate and dithionite, up to decaatomic ions, such as peroxydisulfate, $n = 8$, or tetrathionate, which is a thio analogue of the latter. Not all have a direct X–X bond (e.g., in diphosphate and dichromate an oxygen atom in-

TABLE VIII. Standard Molar Entropies of Gaseous Ions of the Type X_2Y_n ($n \geqslant 4$) at 298.15 K

no.	ion	r_1, nm	r_2, nm	symmetry	$S_i°$(g), J K^{-1} mol^{-1}
85	$C_2O_4^{2-}$	0.156	0.124	D_{2d} or D_{2h}	295.1
86	$S_2O_4^{2-}$	0.2389	0.1505	C_{2v}	319.
87	$S_2O_5^{2-}$	0.2209	0.1499	C_s	335.3
88	$S_2O_6^{2-}$	0.216	0.145	D_{3d}	337.3
89	$S_2O_8^{2-}$	0.146	0.1427	C_{2h} or C_i	341.
90	$S_4O_6^{2-}$	0.2019	0.1457	C_{2h}	356.
91	$P_2O_6^{4-}$	0.2170	0.1502	D_{3d}	341.
92	$P_2O_7^{2-}$	0.1624	0.1507	C_{2v}	342.8
93	$Cr_2O_7^{2-}$	0.178	0.161	C_{2v}	379.7
94	$N_2H_5^+$	0.1462	0.100	C_s	230.5
95	$N_2H_6^{2+}$	0.1439	0.1050	D_{3d}	225.2

tervenes), nor are all symmetrical ($S_2O_5^{2-}$ and $N_2H_5^+$ have an unequal number of Y atoms on the two sides of the X–X group). Hence the symmetry, the number of vibrational frequencies, and their possible degeneracies, differ from one ion to the next and no generalizations can be made. Some of the pertinent data are shown in Table VIII, the other necessary structural and vibrational data are given in the text.

85. Oxalate, $C_2O_4^{2-}$. The symmetry of this ion in the free state has not been definitely established: it may be either coplanar, with symmetry D_{2h}, or nonplanar, the two carboxylate groups being perpendicular to each other, with symmetry D_{2d}. Eleven discrete vibrations should be observed in the first case, and eight in the second, three of which are twofold degenerate. The torsion around the C–C bond is not observable, neither in the infrared nor in the Raman spectrum. Seven or eight vibrations are actually observed for the aqueous ion, and the set used to calculate S_{vib} (ν_1 = 1486, ν_2 = 900, ν_3 = 449, ν_5 = 1519, ν_6 = 524, ν_7 = 1310, ν_9 = 761, ν_{11} = 301, all in cm^{-1}) includes the eight frequencies observed by Begun (1963),[202] where ν_7, ν_9, and ν_{11} are twofold degenerate. These account for the eleven vibrations apart from the torsion mode. The latter has, however, been observed in crystals. The frequency ν_4 = 114, cm^{-1} is that observed and assigned by Shippey (1980)[203] in potassium oxalate. The distances r_1(C–C) and r_2(C–O) and the angle O–C–O = 125° are from Jeffrey (1952),[204] confirmed by Pedersen (1967).[205]

The uncertainties in the distances and angle[205] produce an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{rot}. The uncertainties in S_{vib} are larger, in particular because of the uncertainty in ν_4: in addition to the values reported for potassium oxalate, there are also other values of 92 cm^{-1} and 132 cm^{-1} for lithium and sodium oxalates, respectively.[203] If these are taken as the limits of the possible values for the free ion, they result in a contribution of ±1.5 J K^{-1} mol^{-1} to the uncertainty in S_{vib}. Further contributions arise from conflicting assignments of the other vibrations, e.g., the sets given by Jones (1980)[206] or by Shippey (1980)[207] for aqueous oxalate lead to S_{vib} (less the ν_4 contribution) differing by 1.7 J K^{-1} mol^{-1} from that calculated from the data of Begun (1963).[202] The total uncertainty in $S_i°$(g) is estimated at ±1.8 J K^{-1} mol^{-1}. No value of $S_i°$(g) has been reported previously.

86. Dithionite, $S_2O_4^{2-}$. The geometry of this ion, contrary to that of $C_2O_4^{2-}$, is not open to doubt, since it is definitely bent. Besides the distances r_1(S–S) and r_2(S–O) the structure is characterized by the O–S–O angle, 105.4° (as in sulfite), and the S–S–O angle, 98.7°, as given by Lindquist (1957),[208] in substantial agreement with values given by Dunitz (1956)[209] and Kiers (1978)[210] for $Na_2S_2O_4$ and $ZnS_2O_4 \cdot C_5H_5N$, respectively. Vibrational frequencies have been reported for this ion by Simon (1949),[211] Meyer (1980),[150] and Adams (1980).[212] The latter is the most complete set, but has an overabundance of frequencies, 13, whereas at most 12 are expected for this hexaatomic ion even for the lowest symmetry. If the coupling between the two O–S–O groups is not very large, two bending or deformation vibrations almost coincide, so that even fewer of these frequency values may belong to the $S_2O_4^{2-}$ anion. In fact, the list given by Adams (1980)[212] is the result of the elimination of the Raman lines of impurities from the observed spectrum, so that some of the weaker higher frequency lines should, perhaps, also have been eliminated. Since no definite assignment is given in either of the sources, the following is a tentative assignment used in the calculations (in cm^{-1}): 124 (O_2S–SO_2 torsion), 187 and 229 (OSS deformation), 241 (S–S stretch), 463 (OSS deformation, degenerate), 581 (SO_2 bend, degenerate), and 907, 998, 1019, and 1116 (S–O stretch). Other assignments are possible, and the use of the frequencies from the (incomplete) sets of Simon (1949)[211] and Meyer[150] with a different assumption of degeneracy leads to a value of S_{vib} that differs at most by −4.1 J K^{-1} mol^{-1} from that obtained from the set listed above. The differences in the structural parameters are responsible for a much smaller uncertainty, only ±0.3 J K^{-1} mol^{-1} in S_{rot}. The total uncertainty in $S_i°$(g) is estimated at ±3 J K^{-1} mol^{-1}, no value for this ion having been reported previously.

87. Disulfite, $S_2O_5^{2-}$. This ion exists in equilibrium with HSO_3^- in aqueous solutions but also in solid salts. Its structure has been given by Lindquist (1957)[208] and by Meyer (1979),[213] in good agreement. The anion consists of an SO_3 pyramid as in thiosulfate, bonded via the sulfur to an SO_2 group, r_1 is the S–S distance and r_2 the S–O distance in the SO_2 group, whereas in the SO_3 group it is slightly smaller: 0.1453 nm. The S–S–O (SO_3) angle is 100.5°, the S–S–O (SO_2) angle is 98.5°, the O–S–O (SO_3) angle is 113°, and the O–S–O (SO_2) angle 106° (the S–SO_2 group is not coplanar). Sets of vibrational frequencies have been given by Simon (1956, 1960),[214,215] Devarajan (1977),[216] and Meyer (1979, 1980).[150,213] Fifteen vibrational frequencies with no degeneracies are expected for this heptaatomic ion of low symmetry, and these have been provided in these sets (for the assignments see Devarajan[216]), with some uncertainties due to the presence of foreign ions (e.g., HSO_3^-) in the solutions studied. The set given by Meyer (1979)[213] for a solution is representative: 168, 200, 235, 309, 424, 510, 558, 587, 637, 655, 966, 1052, 1085, 1170, and 1196 cm^{-1}, and leads to the value of $S_i°$(g) in Table VIII. The other sets differ by −1.2 and −2.8 J K^{-1} mol^{-1} for Devarajan's[216] and Simon's,[215] respectively. The uncertainty in S_{rot} is small, ±0.3 J K^{-1} mol^{-1}, so the total uncertainty in $S_i°$(g) is ±1.4 J K^{-1} mol^{-1}. No value of $S_i°$(g) has been reported previously.

88. Dithionate, $S_2O_6^{2-}$. This ion, in contrast with the preceding ones, is of high symmetry and consists of two SO_3 pyramids bonded through their sulfur atoms. The most recent structural data are those of Liminga

(1980),[217] obtained on $Cs_2S_2O_6$, and those of Narayanan (1974)[218] (r_1 is the S–S diatance, r_2 is the S–O distance (Table VIII), and the S-S-O and O-S-O angles are regular tetrahedral in this structure). The uncertainty in S_{rot} due to uncertainties in the structure are ±0.3 J K^{-1} mol^{-1}. Several sets of vibration frequencies are available, and due to the high symmetry, six (ν_7 to ν_{12}) of the eleven observable frequencies are twice degenerate, and a twelfth one (ν_4), the O_3S–SO_3 torsion, is generally not observed. Palmer (1961)[219] has given a set ($\nu_1 = 1102$, $\nu_2 = 710$, $\nu_3 = 293$, $\nu_5 = 1000$, $\nu_6 = 577$, $\nu_7 = 1240$, $\nu_8 = 516$, $\nu_9 = 204$, $\nu_{10} = 1216$, $\nu_{11} = 556$, and $\nu_{12} = 320$, all in cm^{-1}) of frequencies pertaining to the free ion, and this has been adopted by Narayanan.[218] The value of ν_4 has been estimated by Palmer[219] at 154 cm^{-1}, and in fact a band at 160 cm^{-1} has been observed and assigned to ν_4 in the Raman spectrum of solid $K_2S_2O_6$ by Kranzman (1969).[220] Differences in the frequencies reported by these and other authors (e.g., Beattie (1969),[221] Meyer (1980)[150]) are responsible for an uncertainty of ±1.0 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty in $S_i°(g)$ is ±1.1 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

88a. Disulfate, $S_2O_7^{2-}$. Insufficient data have been found for this anion, in order for its $S_i°(g)$ to be calculated, nor has a previous attempt been made. The ion being present in solids, but not in aqueous solution, no value of $\bar{S}_i^{\infty}(aq)$ has been reported either.

89. Peroxydisulfate, $S_2O_8^{2-}$. This ion consists of two SO_4 tetrahedra connected via two oxygen atoms at a distance r_1 apart (see Table VIII), with the two S–O–O angles being 122°, according to Zachariasen (1934).[222] The vibrational frequencies (stretching frequencies: 1303, 1295, 1267, 1262, 1088, 1062, 854, 834 cm^{-1}; bending frequencies: 765, 700, 658, 590, 560–568, 491, 460, 425, 328, 236 cm^{-1}) have been given by Simon (1962),[223] but unfortunately do not constitute a complete set, and no full assignments have been made. Other sets, by Pascal (1951)[224] and Miller (1952)[225] are not complete either, and only 20 out of the required 24 frequencies are known. If accidental degeneracies are introduced for these missing frequencies (bending modes, in the range 425–765 cm^{-1}), the range of the resulting S_{vib} values is 5 J K^{-1} mol^{-1}. The total uncertainty in $S_i°(g)$ is estimated at ±3 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

90. Tetrathionate, $S_4O_6^{2-}$. Although formally this anion is not an ion of the type X_2Y_n, it can still be discussed under this category, if it is considered to be a thio derivative of $S_2O_8^{2-}$, where the two bridging oxygen atoms have been substituted by sulfur ones. The structure as given by Foss (1964),[226] involves in addition to r_1, the length of the central S–S bridge, and r_2, the S–O distance, also the O_3S–S distances of 0.2116 nm, and the following angles: S–S–S 103.8°, O–S–O 113.6°, and S–S–O 107.9°, on the average. The set of vibration frequencies is incomplete, of the 24 values expected only 20 discrete ones are available when the data of Eucken (1948),[227] Gerding (1950),[228] Siebert (1955),[81] Lecomte (1963),[229] and Meyer (1980)[150] are combined. (The frequencies are: 1241, 1215, 1108, 1049, 1042, 1012, 890, 791, 726, 710, 663, 589, 551, 526, 490, 466, 394, 312, 270, and 148 cm^{-1}.) These include assignments for six S–O stretching frequencies, one for the S–S stretching frequencies (two more are needed), and seven of the bending and deformation mode frequencies (eight more are needed). The six unassigned frequencies obviously cover some of those listed above as missing. Accidental coincidences are expected in this ion, according to Gerding (1950),[228] because of the low interaction between the well-separated SO_3 moieties. To estimate the range of uncertainty entailed in S_{vib} the four missing frequencies have been selected to coincide with either the lowest or the highest unassigned ones. The result is ±8 J K^{-1} mol^{-1}. The uncertainty in S_{rot} is due mainly to the uncertainty in the conformation of the S-S-S-S bridge, whether it is cis or trans in the free ion, whatever the preferred conformation in the solid. This uncertainty is ±3.7 J K^{-1} mol^{-1}. No value of $S_i°(g)$ for this ion has been published previously.

91. Hypophosphate, $P_2O_6^{4-}$. This ion is isostructural with dithionate, according to Wilson (1964)[230] and Emmerson (1973),[231] and regular tetrahedral angles are assumed throughout. The P–P distance is r_1 and the P–O one is r_2. The anions have similar sets of vibration frequencies ($\nu_1 = 1062$, $\nu_2 = 670$, $\nu_3 = 275$, $\nu_5 = 942$, $\nu_6 = 562$, $\nu_7 = 1085$, $\nu_8 = 494$, $\nu_9 = 200$, $\nu_{10} = 1168$, $\nu_{11} = 508$, and $\nu_{12} = 325$, those of ν_7–ν_{12} are double degenerate), according to Palmer (1961).[219] The frequency for the O_3P–PO_3 torsion mode, ν_4, however, is observed neither in the Raman nor in the infrared spectrum, and is unknown. In analogy with the relationships between the vibration frequencies of the hypophosphate and dithionate ions, the value $\nu_4 = 140 \pm 30$ is estimated, and this introduces an uncertainty of ±1.7 J K^{-1} mol^{-1} in S_{vib}. An alternative frequency set given by Baudler (1955),[232] leads to an additional uncertainty of ±0.4 J K^{-1} mol^{-1} in S_{vib}. Possible deviations from regular-tetrahedral angles, of up to ±3° according to Wilson (1964),[230] cause an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{rot}, so that the total uncertainty is $S_i°(g)$ is ±1.8 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

92. Diphosphate, $P_2O_7^{4-}$. This ion consists of two PO_3 pyramids connected via an oxygen atom, r_1 being the distance from the P atom to the bridging oxygen atom, r_2 that to a terminal oxygen atom. The angle P–O–P is 132.9°, the O–P–O angle in each PO_3 pyramid is 113.2°, the O–P–O angle between bridging and terminal oxygen atoms is 105.4°, according to Middlemiss (1976),[233] confirming an earlier structure given by McArthur (1957).[234] All 21 vibration frequencies are known, albeit not for the free ion in solution. However, no more than 20 distinct vibrations can be selected from a single source, so that a combination of sources must be used. Such a combination of data from Hezel (1967, 1968)[235] for $Mg_2P_2O_7$ and from Cornilsen (1979)[236] for $Ca_2P_2O_7$ (PO_3 stretches: 1212, 1165, 1140, 1120, 1000, 970; POP stretches: 920, 735; PO_3 bends: 620, 600, 585, 570, 540, 505; OPO(P) bends: 455, 425, 371, 338; torsions: 318, 262, 201, all in cm^{-1}) is representative of the data obtained for various crystal modifications of these salts as well as for $Na_4P_2O_7$. The uncertainties in S_{vib} introduced by the use of different sets of vibrational frequencies are ±0.4 J K^{-1} mol^{-1}, the uncertainties in S_{rot} due to differences in the structural data are ±0.3 J K^{-1} mol^{-1}, and the total uncertainty in $S_i°(g)$ is ±0.5 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

93. Dichromate, $Cr_2O_7^{2-}$. This ion has the same structure as the diphosphate ion discussed above, with

r_1 and r_2 being the distances to the bridging oxygen and terminal oxygen atoms, respectively. The Cr–O–Cr angle is 124°, the O–Cr–O angle is practially the regular-tetrahedral one, according to Brandon (1968).[237] A full set of 21 vibration frequencies is provided by Brown (1972),[238] {130, 150, 255, 329 (accidentally four times degenerate), 370, 377 (accidentally twice degenerate) 386, 390 (accidentally twice degenerate), 560, 764, 893, 905, 925, 935, 954, and 966, all in cm^{-1}}. No additional information, concerning either structural or vibrational data have been found, so that the uncertainties are estimated by arbitrarily assigning a 2% uncertainty to each frequency, distance and angle. The total uncertainty in $S_i°(g)$ is then ±0.8 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

94. Hydrazinium (Monoprotonated), $N_2H_5^+$. The structure of this ion of low symmetry has been given by Golic (1974):[239] r_1 is the N–N distance, r_2 is the mean of the N–H distances (they are somewhat larger in the $-NH_3^+$ part, 0.1019 nm, than in the $-NH_2$ part, 0.0985 nm).

The vibrational frequencies in the solid salts examined depend on the identity of the anion (for the chloride: 531, 975, 1104, 1139, 1255, 1421, 1500 cm^{-1} and further eight frequencies at >1500 cm^{-1}, which do not contribute appreciably to S_{vib}). In particular, the NH_2–NH_3^+ torsion-mode frequency decreases from 568 cm^{-1} in the fluoride, to 531 cm^{-1} in the chloride, to 512 cm^{-1} in the bromide, according to Glavic (1972)[240] and DeVillepin (1974).[241] The chloride salt value has been selected for the calculation, and this is the only substantial contribution to S_{vib}, since all the other frequencies are ≥950 cm^{-1}. The findings of two relatively low frequencies 435 (or 472) cm^{-1} assigned to H_2N–NH_3^+ torsion, and 545 (or 535) cm^{-1}, assigned to NH_2 wag by Schettino (1974)[242] is contrary to the finding of only a single low frequency by the other authors, and is discounted. The uncertainty in S_{vib} is therefore taken to be that due to the effect of the anion, and is ±0.2 J K^{-1} mol^{-1}. The uncertainty in the structural data leads to another ±0.2 J K^{-1} mol^{-1} in S_{rot}, and the total uncertainty in $S_i°(g)$ is ±0.3 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

95. Hydrazinium (Diprotonated), $N_2H_6^{2+}$. The structure of this symmetrical ion is given by Sarin (1977),[243] r_1 being the N–N distance and r_2 the mean N–H distance, the angles being practically the regular-tetrahedral ones. Various sets of vibration frequencies are available (e.g., from Snyder (1959),[244] for the chloride: 455, 1027, 1096 (doubly degenerate), 1105 (doubly degenerate), 1485, 1524 cm^{-1}, and further 10 frequencies at ≥ 1500 cm^{-1}, which do not contribute appreciably to S_{vib}), and as for $N_2H_5^+$, only the ^+H_3N–NH_3^+ torsion mode is significant for the present purpose. The values 521 cm^{-1} for the sulfate, Caville (1977),[245] 455 cm^{-1}, Snyder (1959),[244] or 422 cm^{-1}, Rattcliffe (1981)[246] for the chloride, and 388 cm^{-1}, Rattcliffe,[246] for the bromide, have been reported. The value by Snyder (1959),[244] who has a complete set of 18 frequencies, is used for the calculation, and the uncertainty due to the anion amounts of ±0.8 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty in $S_i°(g)$, taking into account also uncertainties in the structural data, is ±1.0 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been published previously.

G. Octahedral Ions

The early study of the entropies of gaseous ions by Yatsimirskii (1957)[35] included three octahedral ions: AlF_6^{3-}, SiF_6^{2-}, and SnF_6^{2-}. They were tentatively assigned the values of $S_i°(g)$ of the isoelectronic nonionic molecules: SF_6 for the former two and TeF_6 for the latter. Krestov (1968)[7] included additional octahedral ions in his list: $SnCl_6^{2-}$, $SnBr_6^{2-}$, and $PtCl_6^{2-}$, but did not state the sources of the data required for his calculations. Of these ions, only SiF_6^{2-} and $PtCl_6^{2-}$ are sufficiently well characterized in aqueous solutions, to have $S_i^{\infty}(aq)$ values available for them in ref 2. Beside the above there exist many more octahedral ions for which the entropy in the gaseous state can be calculated from known interatomic distances and the vibrational frequencies compiled, e.g., by Nakamoto (1977).[116] In the present study only those that exist as kinetically relatively inert coordination species in aqueous solutions are treated, in addition to those mentioned above.

Fifteen vibrations are expected for XY_6 ions, where the Ys are single atoms, grouped into six modes: ν_1 (nondegenerate), ν_2 (doubly degenerate), ν_3, ν_4, ν_5, and ν_6 (triply degenerate). Because ν_6 is neither Raman nor infrared active it is not observed in general, but can be estimated from ν_5 as $\nu_6 = \nu_5(2^{-1/2})$ according to Nakamoto (1977).[116] When Y is a polyatomic ligand more frequencies are observed, of course. Structurally these ions are characterized by one distance r, from X to a monoatomic Y, whereas polyatomic ligands Y require further distances and, eventually, angles too. The data for a dozen octahedral ions and the resulting $S_i°(g)$ are summarized in Table IX.

96. Hexafluoroaluminate, AlF_6^{3-}. The value of r is given by Brosset (1946)[247] and the vibration frequencies by Reisfeld (1973),[248] except for ν_2 and ν_6. The latter is estimated as $\nu_5(2^{-1/2})$, and for the former there exist estimates of 354 cm^{-1} by Sanyal (1976)[249] and of 400 cm^{-1} by Baran (1981).[250] The uncertainty these discordant estimates introduce in S_{vib} is ±1.3 J K^{-1} mol^{-1}. A possible uncertainty of ±0.005 nm in r produces an uncertainty of ±0.7 J K^{-1} mol^{-1}, so that the total uncertainty in $S_i°(g)$ is ±1.5 J K^{-1} mol^{-1}. The previously reported values of $S_i°(g)$ are 290.8 J K^{-1} mol^{-1}, i.e., the value for the isoelectronic SF_6 (Yatsimirskii[35]) and 295.0 J K^{-1} mol^{-1} (Krestov,[7] with the formula of the ion misprinted as AlF_6^{2-}). These values are much lower than the present one; however their basis, except for the isoelectronic analogy, has not been given. The ion does not exist in aqueous solutions, hence no $S_i^{\infty}(aq)$ is known.

97. Hexafluorosilicate, SiF_6^{2-}. The value of r is from Zalkin (1964),[251] and the vibration frequencies are from Begun (1967),[252] with $\nu_6 = \nu_5(2^{-1/2})$. An alternative set is due to Dean (1967),[253] and the differences lead to an uncertainty of ±0.7 J K^{-1} mol^{-1} in S_{vib}. The uncertainty of ±0.0015 nm in the value of r leads to an uncertainty of only ±0.1 J K^{-1} mol^{-1} in S_{rot}, so that the total uncertainty in $S_i°(g)$ is ±0.7 J K^{-1} mol^{-1}. The values of $S_i°(g)$ given by Yatsimirskii[35] and Krestov[7] are 290.8 and 296.6 J K^{-1} mol^{-1}, respectively, and our comment for AlF_6^{3-} applies here as well.

98. Hexafluorostannate(IV), SnF_6^{2-}. The value of r is from Brown (1965),[254] and the set of vibrational frequencies listed in Table IX is from Begun (1967),[252] with $\nu_6 = \nu_5(2^{-1/2})$. Alternative sets have been given by

TABLE IX. Standard Molar Entropies of Gaseous Octahedral Ions at 298.15 K

no.	ion	r, nm	ν_1, cm^{-1}	ν_2, cm^{-1}	ν_3, cm^{-1}	ν_4, cm^{-1}	ν_5, cm^{-1}	ν_6, cm^{-1}	$S_i°(g)^d$
96	AlF_6^{3-}	0.181	541	450	568	387	322	228^a	329.5
97	SiF_6^{2-}	0.1695	663	477	741	483	408	288^a	309.9
98	SnF_6^{2-}	0.205	592	477	559	300	252	178^a	354.0
99	$RhCl_6^{3-}$	0.2344	302	280	321	200	195	138^a	410.4
100	$PdCl_6^{2-}$	0.232	318	289	346	200	178	126^a	412.2
101	$SnCl_6^{2-}$	0.2427	311	229	303	166	158	112^a	430.2
102	$ReCl_6^{2-}$	0.237	346	275	313	172	159	112^a	426.8
103	$IrCl_6^{3-}$	0.24	323	303	309	200	161	144	416.7
104	$IrCl_6^{2-}$	0.2307	352	225	333	184	196	139^a	421.9
105	$PtCl_6^{2-}$	0.235	348	318	342	183	171	88	425.7
106	$SnBr_6^{2-}$	0.259	190	144	224	118	109	77^a	492.9
107	$Co(CN)_6^{3-}$	0.1894^b	see text						464.8
108	$Fe(CN)_6^{3-}$	0.1936^b	see text						482.5
109	$Fe(CN)_6^{4-}$	0.1900^b	see text						469.8
110	$Co(NH_3)_6^{3+}$	0.1968^c	see text						435.2

[a] $\nu_6 = \nu_5(2^{-1/2})$. [b] The metal-carbon distance, for C-N distance see text. [c] The metal-nitrogen distance.
[d] Units = J K^{-1} mol^{-1}.

several authors, e.g., Wharf (1969),[255] and the resulting uncertainty in S_{vib} is ±1.1 J K^{-1} mol^{-1}. An uncertainty of ±0.005 nm in r causes an uncertainty of ±0.6 J K^{-1} mol^{-1} in S_{rot}, so that the uncertainty in $S_i°(g)$ is ±1.3 J K^{-1} mol^{-1}. The values of $S_i°(g)$ reported by Yatsimirskii[35] and Krestov[7] are 337.6 and 343.5 J K^{-1} mol^{-1}, respectively, and the comment for AlF_6^{3-} applies here again.

99. Hexachlororhodate(III), $RhCl_6^{3-}$. The value of r is from Cresswell (1972),[256] obtained for $K_3RhCl_6 \cdot H_2O$. The frequencies are from Bosworth (1974)[257] (ν_1 and ν_2), Cresswell[256] (ν_3 and ν_4), and Hendra (1967)[258] (ν_5, and $\nu_6 = \nu_5(2^{-1/2})$). Somewhat different values of ν_3 and ν_4, 329 and 187 cm^{-1}, respectively, were given by DeBeau (1969),[259] but the main uncertainty concerns the value of ν_5, since a line observed at 169 cm^{-1} could be assigned to this mode (and then ν_6 would have to be changed accordingly). The total uncertainty in S_{vib} arising from this is ±3.4 J K^{-1} mol^{-1}, which is also the uncertainty in $S_i°(g)$. No value of $S_i°(g)$ has been reported previously.

100. Hexachloropalladate(IV), $PdCl_6^{2-}$. The value of r is estimated from the relative sizes of the Pd^{IV} and Pt^{IV} ions and the corresponding value of r in $PtCl_6^{2-}$. An uncertainty of ±0.005 nm in r causes an uncertainty of ±0.3 J K^{-1} mol^{-1} in S_{rot}. The vibrational frequencies are from DeBeau (1969)[260] (for the ammonium salt). Only the values ν_1–ν_4 are experimental results, those of ν_5 and ν_6 are calculated resulted. A somewhat different set is obtained for the other alkali metal salts, and this leads to an uncertainty of up to ±3.0 J K^{-1} mol^{-1} in S_{vib}. The total uncertainty in $S_i°(g)$ is 3.0 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has previously been reported.

101. Hexachlorostannate(IV), $SnCl_6^{2-}$. The value of r is from Lerbscher (1976)[261] and the vibrational frequencies are from Wharf (1969).[255] The value of r is somewhat sensitive to the alkali metal cation that accompanies the $SnCl_6^{2-}$ anion in the salt examined,[255,262] but the range of values, ±0.002 nm, has only a small effect on S_{rot}, ±0.1 J K^{-1} mol^{-1}. Several alternative sets of vibrational frequencies are available, depending, again, on the accompanying cation in the solid salt or on the presence of the $SnCl_6^{2-}$ ion in an aqueous solution with excess hydrochloric acid. The studies of DeBeau (1967),[263] Bosworth (1974)[257] and Donaldson (1975)[264] illustrate this point, in particular with regards to ν_5 (hence also of $\nu_6 = \nu_5(2^{-1/2})$, for which values varying from 157 to 176 cm^{-1} have been found. The uncertainty of S_{vib} is, thus, ±1.8 J K^{-1} mol^{-1}, as is also the total uncertainty in $S_i°(g)$. The value of $S_i°(g)$ reported by Krestov,[7] 359.8 J K^{-1} mol^{-1}, is much lower than the present value, and, as noted above, without documentation of the source of the data used for its calculation.

102. Hexachlororhenate(IV), $ReCl_6^{2-}$. The value of r is from Aminoff (1935)[265] and the vibration frequencies are from Hendra (1967).[258] Alternative sets of ν_1, ν_2, and ν_5 (hence also $\nu_6 = \nu_5(2^{-1/2})$) are available from Bosworth (1974)[257] and Woodward (1964),[266] but since these differ only little from the former set, the total uncertainty of $S_i°(g)$ is estimated to be no larger than ±0.3 J K^{-1} mol^{-1}. No value of $S_i°(g)$ has been reported previously.

103. Hexachloroiridate(III), $IrCl_6^{3-}$. The magnitude of r is a rough estimate, since no reliable value has been found. The frequencies are from Bottger (1972),[267] and it should be noted that ν_6 deviates considerably from $\nu_5(2^{-1/2})$. Somewhat different values for ν_1 and ν_2 have been given by Bosworth (1974)[257] (ν_4 = 315 cm^{-1}, ν_2 = 296 cm^{-1}) and by Cresswell (1972)[256] (ν_4 = 185). The uncertainty in S_{vib} arising from these alternative sets of frequencies is ±0.9 J K^{-1} mol^{-1}, that in S_{rot} arising from a possible uncertainty of ±0.005 nm in r is ±0.3 J K^{-1} mol^{-1}, so that the total uncertainty in $S_i°(g)$ is ±1.0 J K^{-1} mol^{-1}.

104. Hexachloroiridate(IV), $IrCl_6^{2-}$. The value of r is from Lindop (1970),[268] obtained for K_2IrCl_6. The frequencies are from Brown (1970)[269] (with $\nu_6 = \nu_5(2^{-1/2})$). A single unpaired electron in this complex contributes R ln 2 to $S_i°(g)$. Alternative values of the frequencies have been given by Kelly (1972)[270] (ν_3 = 311 cm^{-1}, ν_4 = 180 cm^{-1}), by Bosworth (1974)[257] (ν_1 = 346 cm^{-1}, ν_2 = 293 cm^{-1}, ν_5 = 160 cm^{-1}), and by Bottger (1972)[267] (ν_2 estimated at 290 cm^{-1}, ν_4 = 188 cm^{-1}). The main discrepancy is in ν_2, and is the major contribution to the uncertainty of S_{vib} {and of $S_i°(g)$} of ±2.8 J K^{-1} mol^{-1}.

105. Hexachloroplatinate(IV), $PtCl_6^{2-}$. The value of r is from Engel (1935)[262] and the set of vibrational frequencies is from DeBeau (1967, 1969),[259,263] and specifically for the potassium salt. Here, again, the vibrational frequencies are sensitive to the accompanying cation or to the aqueous environment, as is illustrated by the data of DeBeau,[259,263] Bosworth (1974),[257] Woodward (1967),[271] Adams (1967),[272] Hendra (1967),[258] among others. The main discrepancies, again, are in ν_5, ranging from 160 to 184 cm^{-1} and in ν_6, where the value 65 cm^{-1} has been determined by Adams (1967)[272] in the $(C_2H_5)_4N^+$ salt, whereas calculated values range from 82 to 124 cm^{-1}[260] (seriously deviating from the estimate $\nu_6 = \nu_5(2^{-1/2})$). These large ranges introduce a considerable uncertainty in S_{vib}, but if the concern is limited to the frequencies of the free anion, i.e., that in aqueous solutions, the range of ν_5 reduces to 160–162 cm^{-1}. This is a more appropriate range of uncertainty for the present purpose, since the cation effects are beyond the present considerations. The uncertainty in r, from determinations on different alkali metal salts, is ±0.001 nm, leading to an uncertainty of ±0.1 J K^{-1} mol^{-1} in S_{rot}, those in ν for aqueous solutions lead to an uncertainty of ±0.6 J K^{-1} mol^{-1} in S_{vib}, which is also the total uncertainty in $S_i°(g)$. The value of $S_i°(g)$ reported by Krestov (1968),[7] 336.0 J K^{-1} mol^{-1}, is much lower than the present value, again with no documentation on how it has been arrived at.

106. Hexabromostannate(IV), $SnBr_6^{2-}$. The value of r is from Ketelaar (1937)[273] and the set of vibrational frequencies is from DeBeau (1967).[263] The sensitivity of r to the alkali metal counterion accompanying the $SnBr_6^{2-}$ anion in the salt leads via an uncertainty of ±0.002 nm to an uncertainty of ±0.1 J K^{-1} mol^{-1} in S_{rot}. The sensitivity of the frequencies, and in particular ν_5 (and $\nu_6 = \nu_5(2^{-1/2})$), which ranges from 94 to 110 cm^{-1}, leads to an uncertainty of ±4 J K^{-1} mol^{-1} in S_{vib}. If only the values obtained for the free ion, i.e., that in aqueous solutions, as reported by Bosworth (1974)[257] and Anthonsen (1974),[274] are considered, the range is only from 94 to 101 cm^{-1} or ±1.7 J K^{-1} mol^{-1} in S_{vib}, which is also the estimated uncertainty in $S_i°(g)$. The value reported by Krestov,[7] 426.3 J K^{-1} mol^{-1}, is, again, much lower than the present value, but with no documentation on how it has been arrived at.

107. Hexacyanocobaltate(III), $Co(CN)_6^{3-}$. The value of r, the Co–C distance, is from Armstrong (1973),[275] in good agreement with that given by Reynhardt (1972),[276] but the corresponding C–N distances are somewhat different: 0.1179 and 0.1163 nm, respectively. The 33 vibrational degrees of freedom required for this 13-atom ion are grouped into 13 modes, of which ν_1 and ν_2 are nondegenerate, ν_3 and ν_4 are doubly degenerate, and the rest are triply degenerate. Because of symmetry considerations for this O_h-type ion, none of ν_5, ν_{12}, and ν_{13} are observed as fundamentals in either the Raman or the infrared spectrum, but they may be observed as combination bands in certain solids. The set of frequencies selected for the present purpose ($\nu_1 = 2151$, $\nu_2 = 411$, $\nu_3 = 2137$, $\nu_4 = 391$, $\nu_5 = 355$, $\nu_6 = 2127$, $\nu_7 = 565$, $\nu_8 = 416$, $\nu_9 = 115$, $\nu_{10} = 482$, $\nu_{11} = 115$, $\nu_{12} = 437$, and $\nu_{13} = 104$, all in cm^{-1}) is based primarily on those observed in aqueous solutions by Swanson (1971),[277] complemented by ν_4 and ν_5 observed for the same medium by McAllister (1970),[278] by ν_{12} for solid $Cs_2LiCo(CN)_6$ of Armstrong (1973),[275] and by ν_{13} for solid $K_3Co(CN)_6$ of Nakagawa (1973).[279] These observed values have been preferred over values calculated from force constants, especially for ν_{13}, but also for ν_9, where the values observed in solid salts are considerably higher. The necessity to distinguish between lattice vibrations and skeletal vibrations in the spectra of the solid salts is particularly severe in the present case, where some of the latter frequencies are rather low. The assignment of the 72–73 and 94–95 cm^{-1} lines observed in $K_3Co(CN)_6$ to lattice vibrations, and not to C–Co–C deformations, by Nakagawa (1973)[279] is accepted by us, in view of the value of $\nu_{13} = 137$ cm^{-1} obtained from a combination line of $Cs_2LiCo(CN)_6$ by Armstrong (1973)[275] and the $\nu_9 = 115$ cm^{-1} obtained for aqueous solutions by Swanson (1971).[277] The earlier assignment of these very low frequencies to ν_{13} and ν_9, respectively by Jones (1962)[280] and by Nakagawa (1962),[281] on the basis of force constant calculations, is therefore rejected. There are small differences in other frequencies reported by various authors, and these lead in combination to an uncertainty of ±3.0 J K^{-1} mol^{-1} in S_{vib}. The slight discrepancy in the bond lengths noted above leads to an uncertainty in S_{rot} which is negligible compared to that in S_{vib}, which is then the uncertainty in $S_i°(g)$ too. No value of $S_i°(g)$ has been reported previously.

108. Hexacyanoferrate(III), $Fe(CN)_6^{3-}$. The value of r, the Fe–C distance, is from Armstrong (1973),[275] and the corresponding C–N distance is 0.1191 nm. The vibrational frequencies are very similar to those for hexacyanocobaltate(III) ($\nu_1 = 2131$, $\nu_2 = 388$, $\nu_3 = 2124$, $\nu_4 = 363$, $\nu_5 = 316$, $\nu_6 = 2123$, $\nu_7 = 516$, $\nu_8 = 397$, $\nu_9 = 129$, $\nu_{10} = 417$, $\nu_{11} = 102$, $\nu_{12} = 380$, and $\nu_{13} = 100$, all in cm^{-1}). They have been taken mainly from Adams (1972),[282] as far as available for aqueous solutions, otherwise from Nakagawa (1970),[283] and ν_4 from Armstrong (1973).[275] The C–N stretching frequencies ν_1, ν_3, and ν_6 are all >2000 cm^{-1} and contribute negligibly to S_{vib}. The frequencies ν_2, ν_4, ν_5, ν_7, ν_8, ν_{10}, and ν_{12} are in the range 300–600 cm^{-1}, and uncertainties in them are of consequence. The values for solid $K_3Fe(CN)_6$ are sufficiently near those in aqueous solutions to be good substitutes, but those for solid $Cs_2LiFe(CN)_6$ are generally appreciably higher, and are not used. These vibrations lead to an uncertainty of ±1.5 J K^{-1} mol^{-1} in S_{vib}. Even more serious are uncertainties in the C–Fe–C deformation modes, ν_9, ν_{11}, and ν_{13}, due to the low frequency values. The values used in the computations are the calculated values of Nakagawa (1979).[283] These are corroborated by the measured values of Dunsmuir (1971)[284] on solid $K_3Fe(CN)_6$, but differ from those measured by Bloor (1964)[285] on the same salt. The discrepancies in ν_9, ν_{11}, and ν_{13} amount to ±4.0 J K^{-1} mol^{-1}. Since the uncertainty in S_{rot} is relatively negligible, the uncertainty in $S_i°(g)$ is ±4.3 J K^{-1} mol^{-1}. $Fe^{III}(CN)_6^{3-}$ has an unpaired electron, hence $R \ln 2$ should be added to $S_{tr} + S_{rot} + S_{vib}$ to give $S_i°(g)$. No value of $S_i°(g)$ has been reported previously.

109. Hexacyanoferrate(II), $Fe(CN)_6^{4-}$. The value of r, the Fe–C distance, is from Swanson (1974),[286] and the corresponding C–N distance, 0.1138 nm, is from the same source. The vibration frequencies, again, are similar to those of $Co(CN)_6^{3-}$, see above ($\nu_1 = 2094$, $\nu_2 = 393$, $\nu_3 = 2058$, $\nu_4 = 410$, $\nu_5 = 350$, $\nu_6 = 2030$, $\nu_7 = 585$, $\nu_8 = 414$, $\nu_9 = 129$, $\nu_{10} = 509$, $\nu_{11} = 93$, $\nu_{12} = 380$, and $\nu_{13} = 100$, all in cm^{-1}). Those observed for aqueous solutions are from Swanson (1976)[287] (ν_1–ν_4, ν_{10} and ν_{11}) and others are for the solid $K_4Fe(CN)_6 \cdot 3H_2O$ obtained from Nakagawa (1962),[281] except for ν_9, ν_{12}, and ν_{13}. For the latter the corresponding values for $Fe(CN)_6^{3-}$ have been taken, there being no observed values available. The values for ν_1, ν_2, ν_3, ν_{10}, and ν_{11} given here for aqueous solutions are in agreement with those given for this medium by Griffith (1970),[288] the main uncertainty arising from ν_{11} (105 cm^{-1} according to the latter). The vibrations observed in the solid, ν_5, ν_6, ν_7, and ν_8, also are in good agreement among the authors. However, no observed values for ν_{12} and ν_{13} could be found, and the one found for ν_9, 225 cm^{-1} in solid $Cs_2MgFe(CN)_6$, deviates from all reasonable estimates for the free ion. The values estimated by Nakagawa (1962)[281] for these frequencies ($\nu_9 = 95$, $\nu_{12} = 402$, $\nu_{13} = 72$, all in cm^{-1}) are sufficiently different from those used here to cause a serious discrepancy of 14.7 J K^{-1} mol^{-1} in S_{vib}. Since Nakagawa (1973)[279] has revised his earlier estimates (1962)[281] concerning the assignments of some low frequencies of $Co(CN)_6^{3-}$ to lattice vibrations rather than to sekeltal modes, it is likely that his estimates for ν_9 and ν_{10} are too low, but on the other hand, the values taken from $Fe(CN)_6^{3-}$ and used here may be too high. It is reasonable to expect the true values to lie somewhere in between, so that $S_i°(g)$ may be some 7 J K^{-1} mol^{-1} larger than that given in Table IX, and its uncertainty may be ±7 J K^{-1} mol^{-1}, or so. No value of $S_i°(g)$ has been reported previously.

110. Cobalt(III) Hexaammine, $Co(NH_3)_6^{3+}$. The value of r, the Co–N distance, is from Kruger (1978),[289] in good agreement with that given by Meek (1970).[290] For the purpose of the calculation of S_{rot}, each ammonia molecule is considered as a "heavy" nitrogen atom, located along the Co–N axis at the center of gravity of the NH_3 ligand. For this purpose the average length of an N–H bond, 0.100 nm, is used. Since an O_h symmetry can be ascribed to this complex ion only if the NH_3 ligands are considered as moieties that are freely rotating around the Co–N bonds, there is an additional contribution to S_{rot} from the six degrees of freedom of these rotators. For the 25-atom molecular ion there remain, then, 75 - 6 - 6 = 63 degrees of freedom for vibrations. Of these, 15 pertain to the CoN_6 skeleton, and the rest to the ammonia ligands. The former set is divided among six modes of the same degeneracies as for octahedral complexes with monoatomic ligands. These are ν_1 (nondegenerate) = 490 cm^{-1}, ν_2 (twice degenerate) = 440 cm^{-1}, ν_3 (split into three frequencies) = 449, 477, and 498 cm^{-1}, ν_4 and ν_5 (three times degenerate) = 331 and 317 cm^{-1}, respectively, and ν_6 (three times degenerate, not observed) = $\nu_5(2^{-1/2})$ = 224 cm^{-1} [see Sanyal (1976)[291]]. Of these, ν_1, ν_2, ν_3, and ν_5 are taken from Raman spectroscopic observations of Siebert (1969)[292] on aqueous solutions, and ν_4 from infrared data on solid $Co(NH_3)_6Cl_3$ of Schmidt (1974),[293] since it is not observed in the Raman spectrum of the solution.

Of the 48 vibrations associated with the ammonia ligands, there are two groups (rocking vibrations) at 830 and 833 cm^{-1}, two at 1327 and 1335 cm^{-1}, and two at 1620 and 1580 cm^{-1}. Each line is three times degenerate, the former line in each group is observed in the infrared spectrum of the solid salt and the latter in the Raman spectrum of the solution. The latter source gives also a nondegenerate line at 1417 cm^{-1}. Not observed, due to the selection rules, are two further modes (triply degenerate each) of the rocking vibration of the ammonia ligand. It is assumed that they would also have frequencies of 830 cm^{-1}, similar to the observed ones, with an estimated uncertainty of ±50 cm^{-1}. There is in addition a multitude of frequencies >1620 cm^{-1}, some observed and some not, but their total contribution S_{vib} is altogether negligible.

The main uncertainty in S_{vib} arises from the value of ν_6, calculated as $\nu_5(2^{-1/2})$, where a probable error of ±10 cm^{-1} causes an uncertainty of ±0.9 J K^{-1} mol^{-1}, and small differences in the frequencies reported by various authors for aqueous solutions, e.g., Swaddle (1970),[294] or for solid salts, e.g., Siebert (1969),[292] Swaddle,[294] Long (1970),[295] among others. These differences account for another uncertainty of ±1.3 J K^{-1} mol^{-1}, so the total uncertainty in S_{vib} is ±1.6 J K^{-1} mol^{-1}. The uncertainty in S_{rot} is negligible compared with that in S_{vib}, so that the latter is taken as the uncertainty in $S_i°(g)$. No value of $S_i°(g)$ has been reported previously.

H. Miscellaneous Ions

The requirement that all the vibrational frequencies be known limits the possibility of calculating the entropies of ions in the gaseous state to relatively small molecular ions. Apart from the formate and oxalate ions dealt with above, the simplest organic ions capable of existence in aqueous solutions are acetate and methylammonium which have 7 and 8 atoms and require 15 and 18 frequency values, respectively. A further complication that arises is the necessity to know the height of the barrier for the rotation of one part of the molecule relative to another. In the cited examples this is the rotation of the methyl group around the C–C and the C–N bond, respectively. In previous encounters of this problem in this paper, the rotation has been treated in some cases as a torsional vibration (e.g., for oxalate or dithionate), in other cases as an internal free rotation (e.g., for platinum(II) tetraammine or cobalt(III) hexaammine). Each case must be discussed individually, in the light of the information available.

In this review only a few representative organic ions will be discussed: acetate, trifluoroacetate, hydroxyammonium, methylammonium, and tetramethylammonium. Although the standard partial molar entropies of other aqueous alkylammonium ions have been reported, and some of the entropies of the gaseous ions too,[296] the vibrational frequency data basis for these further ions is inadequate.

111. Acetate, $CH_3CO_2^-$. The structural data are from Wei (1977),[297] with the C–C distance being 0.1505 nm, the C–O distance 0.127 nm, the C–H distance 0.1095 nm, the $C\text{–}C(O_2)$ group coplanar with an O–C–O angle of 120°, and the H–C–H angles regular tetrahedral. The symmetry is C_s, and 15 nondegenerate vibrational frequencies are expected. Of these only five are <1000 cm^{-1} with appreciable contributions to S_{vib}, including the ν_{15} $H_3C\text{–}CO_2^-$ torsional vibration. A recent set of frequencies ($\nu_1 = 3001$, $\nu_2 = 2934$, $\nu_3 = 1584$, $\nu_4 = 1440$, $\nu_5 = 1420$, $\nu_6 = 1334$, $\nu_7 = 1012$, $\nu_8 = 924$, $\nu_9 = 651$, $\nu_{10} = 462$, $\nu_{11} = 2983$, $\nu_{12} = 1440$, $\nu_{13} = 1044$, $\nu_{14} = 622$, and $\nu_{15} = 204$, all in cm^{-1}, the 1420–1440 band not being well resolved) is given by Kakihana (1983),[298] in substantial agreement with earlier sets, e.g., that of Kotov (1968),[299] except for the torsional vibration ν_{15} which is not observed in the infrared spectrum reported by the latter authors. A tentative assignment of this frequency is given by Spinner (1964)[300] from Raman spectroscopic data: 247 cm^{-1} (or perhaps the 228 cm^{-1} line), but a definite value of ν_{15} = 204 cm^{-1} is given by Kakihana (1982)[298] on the basis of ^{13}C spin–lattice relaxation-time measurements. The value of $S_i°(g)$ calculated on this basis is 278.7 J K^{-1} mol^{-1}.

The uncertainties in the intramolecular distances and angles are minimal, and lead to an uncertainty of ±0.1 J K^{-1} mol^{-1} in S_{rot}. Those in the vibrational frequencies, except for ν_{15}, lead to only another ±0.1 J K^{-1} mol^{-1} in S_{vib}, but the uncertainty in ν_{15} is difficult to estimate. If the two extreme estimates given above are used to delimit the uncertainty it is ±0.8 J K^{-1} mol^{-1}, and the total uncertainty in $S_i°$(g) is also ±0.8 J K^{-1} mol^{-1}. No value of $S_i°$(g) has been reported previously.

112. Trifluoroacetate, $CF_3CO_2^-$. Structural data for this anion have been examined by Brown (1980),[301] and an "idealized" structure has been proposed, that fits the experimental data for most salts. It has C–C, C–O, and C–F distances of 0.154, 0.124, and 0.129 nm respectively, an O–C–O angle of 128°, and a regular-tetrahedral arrangement of the atoms in the C–CF_3 grouping. The vibrational frequencies have been given by Christie (1973)[302] for the Raman spectrum of an aqueous solution of the sodium salt: ν_1 = 1438, ν_2 = 1206, ν_4 = 844, ν_5 = 810, ν_6 = 727, ν_7 = 598, ν_8 = 409, ν_{10} = 1680, ν_{11} = 1145, ν_{12} = 520, ν_{13} = 434, and ν_{14} = 266, all in cm^{-1}. These authors also reported values for frequencies not observed in this spectrum: ν_3 = 1188 cm^{-1} and ν_9 = 224 cm^{-1} for trifluoroacetate from Spinner (1964),[300] and ν_{15} = 50 cm^{-1} for trifluoroacetyl fluoride (which is isoelectronic with the trifluoroacetate anion) from Berney (1971).[303] These frequencies are confirmed by the more recent study of Regis (1979),[304] except for ν_9 and ν_{15} that are not reported in this publication.

If the value ν_{15} = 50 cm^{-1} for the torsion around the C–C bond obtained for CF_3COF is taken to represent also this torsion frequency for $CF_3CO_2^-$, then the calculated entropy for the gaseous anion is 330.6 J K^{-1} mol^{-1}. This constitutes the major uncertainty, since if this frequency is assumed to be as low as 35 cm^{-1} or as high as 75 cm^{-1} for the charged anion, $S_i°$(g) = 333.6 or 327.3 J K^{-1} mol^{-1} results, respectively. If it is assumed that free rotation around the C–C bond takes place, the difficulty of assigning a symmetry number arises, which would be 2 if the CF_3 group is taken to rotate vs. the CO_2 plane, or 3 if the CO_2 group is taken to rotate vs. the CF_3 pyramid. The values of $S_i°$(g) resulting from these options are 357.1 and 353.7 J K^{-1} mol^{-1}, respectively. The interpretation in terms of a definite (though for the anion not exactly known) torsional frequency is preferred over that of the free rotation, so that $S_i°$(g) = 331 ± 3 J K^{-1} mol^{-1} is accepted.

113. Hydroxyammonium, NH_3OH^+. The ion consists of a pyramidal NH_3 group having regular tetrahedral angles and N–H bond lengths of 0.1044 nm, attached to an OH group with an N–O bond length of 0.1383 nm. The OH bond is 0.0996 nm long and at a dihedral angle of 53.6° between the HON and ONH planes according to Padmanabhan (1967).[305] The vibration frequencies are nondegenerate; ν_1 = 3152, ν_2 = 1187, ν_3 = 535, ν_4 = 3005, ν_5 = 1460, ν_6 = 994, and practically double degenerate; ν_7 = 3046, ν_8 = 1568, ν_9 = 1152, all in cm^{-1}, from Frasco (1959),[306] obtained on solid NH_3OHBr, with a symmetry class C_1. The frequency ν_3 corresponds to the torsion around the N–O bond, and is sensitive to the anion in the solids examined by inelastic neutron scattering by Jayasooriya (1981).[307] It is as high as 875 cm^{-1} for the (hydrogen-bonded) F$^-$ salt, and as low as 460 cm^{-1} for the (practically non-hydrogen-bonded) I$^-$ salt. The value of $S_i°$(g) = 235.4 J K^{-1} mol^{-1} obtained from these data has an uncertainty of ±0.6 J K^{-1} mol^{-1}. An uncertainty of ±0.4 J K^{-1} mol^{-1} in S_{rot} is contributed from the uncertainties in the distances and angles, and in particular in the position of the OH bond with respect to the NH_3 pyramid, considered as rigid. A similar uncertainty in S_{vib} is contributed mainly from the uncertainty in ν_3, due to the anion effect, considering only the bromide and iodide salts, with minimal hydrogen bonding. No value of $S_i°$(g) has been reported previously.

114. Methylammonium, $CH_3NH_3^+$. This ion has C_{3v} symmetry, with both parts having a regular-tetrahedral structure. The distances used are C–N 0.150 nm, C–H 0.109 nm, and N–H 0.103 nm. The eighteen vibrational frequencies are grouped into six nondegenerate and six doubly degenerate modes of which the nondegenerate ν_6, corresponding to the H_3C–NH_3^+ torsion, is inactive in both Raman and infrared spectra. A recent set of frequencies (ν_1 = 2980, ν_2 = 2962, ν_3 = 1530, ν_4 = 1433, ν_5 = 999, ν_7 = 3086, ν_8 = 3021, ν_9 = 1556, ν_{10} = 1463, ν_{11} = 1253, ν_{12} = 959, all in cm^{-1}; ν_7–ν_{12} are doubly degenerate) is given by Meinander (1981)[309] from Raman spectroscopic measurements on solid CH_3NH_3Cl. It is in good agreement with an earlier set by Theoret (1967),[310] based on the infrared spectrum. Both of these sets lack a value for ν_6, which is supplied by the inelastic neutron scattering work of Ludman (1967),[308] giving ν_6 = 264 cm^{-1} for the free ion, equated with the value observed for the hexafluorophosphate salt, where hydrogen bonding in the solid salt should be minimal. A similar value, ν_6 = 268 cm^{-1}, has been given for the β phase of the chloride salt from Raman spectroscopic observations of Forss (1976).[311] The value of $S_i°$(g) calculated on this basis is 232.7 J K^{-1} mol^{-1}.

Uncertainties of ±0.002 nm in the structural parameters lead to an uncertainty of ±0.2 J K^{-1} mol^{-1} in S_{rot}. Since all of the vibration frequencies, except for ν_6, are >900 cm^{-1}, uncertainties in them are immaterial and produce an uncertainty of <0.1 J K^{-1} mol^{-1} in S_{vib}. The value of ν_6 observed by inelastic neutron scattering depends on the anion of the solid methylammonium salt. The values for the chloride and bromide bracket that for the hexafluorophosphate, used to represent the free ion.[308] If these are used as a measure of the uncertainty in ν_6, the resulting uncertainty in S_{vib} is ±0.5 J K^{-1} mol^{-1}. The total uncertainty in $S_i°$(g) is thus estimated at ±0.6 J K^{-1} mol^{-1}. No value of $S_i°$(g) has been reported previously.

115. Tetramethylammonium, $(CH_3)_4N^+$. For the purpose of the calculation of the rotational entropy, this ion has been considered as a regular tetrahedron, with a symmetry number of 12 and with a central nitrogen ion and four peripheral "heavy" carbon atoms, having the mass of a methyl group and being located at the centers of gravity of the methyl groups. The rotations of the methyl groups around the N–C bonds should then be treated as free rotations. On the other hand, these rotations may have finite potential barriers with definite vibration frequencies assigned to them and the symmetry number for the rotation in this "rigid" configuration can be as low as unity, although the moments of inertia can still be calculated on the same basis.

The molecular structure of the ion is regular tetrahedral for both the NC_4 skeleton and the NCH_3 moie-

TABLE X. Extrapolation Table for $S_{vib}(T)$. Vibrational Contributions to the Entropy (J K^{-1} mol^{-1}) at 0-300 °C[a]

ν	$T = 273$	$T = 298$	$T = 323$	$T = 348$	$T = 373$	$T = 423$	$T = 473$	$T = 523$	$T = 573$
40	21.28	22.00	22.67	23.29	23.86	24.91	25.84	26.67	27.43
60	17.93	18.65	19.31	19.93	20.50	21.55	22.47	23.30	24.06
80	15.56	16.28	16.94	17.55	18.13	19.16	20.09	20.92	21.68
100	13.74	14.45	15.11	15.72	16.29	17.32	18.24	19.07	19.83
120	12.27	12.97	13.62	14.23	14.80	15.83	16.74	17.57	18.32
140	11.03	11.73	12.38	12.98	13.54	14.56	15.48	16.30	17.05
160	9.98	10.67	11.31	11.90	12.46	13.48	14.39	15.21	15.95
180	9.06	9.74	10.37	10.96	11.52	12.52	13.43	14.24	14.99
200	8.26	8.92	9.55	10.13	10.68	11.68	12.58	13.39	14.13
220	7.54	8.20	8.81	9.39	9.93	10.92	11.81	12.62	13.36
240	6.90	7.54	8.15	8.72	9.25	10.23	11.12	11.92	12.65
260	6.32	6.95	7.55	8.11	8.63	9.60	10.48	11.28	12.01
280	5.80	6.42	7.00	7.55	8.07	9.03	9.90	10.69	11.41
300	5.32	5.93	6.50	7.04	7.55	8.50	9.36	10.14	10.87
350	4.31	4.88	5.42	5.93	6.43	7.34	8.18	8.95	9.65
400	3.50	4.03	4.53	5.02	5.49	6.37	7.18	7.93	8.62
450	2.85	3.33	3.80	4.26	4.70	5.54	6.33	7.05	7.73
500	2.31	2.75	3.19	3.62	4.04	4.84	5.59	6.29	6.95
550	1.879	2.28	2.68	3.07	3.47	4.22	4.94	5.62	6.26
600	1.524	1.881	2.25	2.61	2.98	3.69	4.38	5.03	5.65
650	1.234	1.553	1.883	2.22	2.56	3.23	3.88	4.51	5.11
700	0.998	1.281	1.578	1.885	2.20	2.83	3.44	4.04	4.62
750	0.806	1.055	1.321	1.600	1.887	2.47	3.06	3.63	4.18
800	0.650	0.867	1.105	1.357	1.619	2.16	2.71	3.26	3.79
850	0.523	0.712	0.923	1.149	1.388	1.889	2.40	2.92	3.43
900	0.420	0.584	0.770	0.973	1.189	1.651	2.13	2.62	3.11
950	0.337	0.478	0.641	0.822	1.018	1.441	1.891	2.35	2.81
1000	0.270	0.391	0.534	0.695	0.871	1.258	1.676	2.11	2.55
1100	0.173	0.261	0.369	0.494	0.635	0.956	1.315	1.697	2.09
1200	0.110	0.173	0.253	0.350	0.462	0.725	1.030	1.363	1.715
1300	0.069	0.114	0.173	0.247	0.335	0.548	0.804	1.093	1.404
1400	0.044	0.075	0.118	0.174	0.242	0.413	0.627	0.875	1.148
1500	0.027	0.049	0.080	0.122	0.174	0.311	0.488	0.699	0.937
1600	0.017	0.032	0.054	0.085	0.125	0.233	0.379	0.557	0.764
1700	0.011	0.021	0.037	0.059	0.090	0.175	0.293	0.444	0.622
1800	0.007	0.014	0.025	0.041	0.064	0.130	0.227	0.353	0.505
1900	0.004	0.009	0.017	0.029	0.046	0.097	0.175	0.280	0.410
2000	0.003	0.006	0.011	0.020	0.032	0.072	0.135	0.222	0.332

[a] Temperatures T in K and vibration frequencies ν in cm^{-1}.

ties. The distances, according to Boyd (1969),[312] are 0.150 nm for the C–N and 0.109 nm for C–H bonds. The 45 vibrations expected for this 17-atom ion are grouped into 4 nondegenerate modes, 4 doubly degenerate modes, and 11 triply degenerate modes. One nondegenerate (ν_4) and one triply degenerate (ν_{12}) vibration correspond to torsions of the four methyl groups around the N–C bonds. The other frequencies have been reported by several authors, but with differing assignments. A set of frequencies is combined here from those given by Kabisch (1980),[313] Anhouse (1972)[314] (extensive sets), Harmon (1974)[315] and Agashe (1979)[316] (less extensive ones), taking into account the nonclashing assignments given by the authors, and in analogy with assignments given for methylammonium by Meinander (1981).[309] ($\nu_1 = 2823$, $\nu_2 = 1448$, $\nu_3 = 752$, ($\nu_4 = 294$) (nondegenerate), $\nu_5 \geq 2800$, $\nu_6 = 1469$, $\nu_7 = 1179$, $\nu_8 = 380$ (doubly degenerate), $\nu_9 \geq 2800$, $\nu_{10} = 1488$, $\nu_{11} = 1076$, ($\nu_{12} = 363$), $\nu_{13} = 3030$, $\nu_{14} = 2785$, $\nu_{15} = 1500$, $\nu_{16} = 1449$, $\nu_{17} = 1287$, $\nu_{18} = 948$, and $\nu_{19} = 456$ (triply degenerate), all in cm^{-1}; the frequencies ν_4 and ν_{12} correspond to $(CH_3)_3N–CH_3$ torsions.)

The value $S_{rot} = 85.19$ J K^{-1} mol^{-1} is obtained on the basis of T_d symmetry, but if the "rigid" configuration is assumed, the symmetry is no longer T_d, and the symmetry number in the calculation of S_{rot} is 1 rather than 12. This adds a term of 20.66 J K^{-1} mol^{-1} to the skeletal S_{rot} (assuming the "heavy C atoms" in lieu of CH_3 groups). The frequencies of the torsions, $\nu_4 = 294$ cm^{-1} (nondegenerate) and $\nu_{12} = 363$ cm^{-1} (triply degenerate) have been given by Rattcliffe (1976),[317] and they contribute together 20.00 J K^{-1} mol^{-1} to S_{vib}. The total contribution from the torsional vibrations, is thus 40.7 J K^{-1} mol^{-1}. A similar result is obtained if this contribution is calculated as a hindered rotation according to the procedure given by Pitzer and Brewer (ref 8, pp 438–440) using the Tables 27-12 and 27-13 given there for iterpolation. The resulting $S_i°(g)$ is 331.9 J K^{-1} mol^{-1}.

If, instead, free rotation of the methyl groups is assumed, these four vibrations are regarded as rotations, the symmetry is T_d, the symmetry number is 12, and four terms of 15.04 J K^{-1} mol^{-1} per methyl group rotation are added to S_{rot}, altogether 60.2 J K^{-1} mol^{-1}, leading to a value of 351.4 J K^{-1} mol^{-1} for $S_i°(g)$. This value is rejected, however, for the following reason. The barrier V_0 to free rotation, estimated from the relationship[318]

$$\nu_t = (V_0 A_1 A_2 / A)^{1/2}$$

where A, A_1, and A_2 are the rotational constants of the whole molecular ion and the two rotating parts ($-CH_3$ and $-N(CH_3)_3$), respectively, is about 2600 cm^{-1} (a weighted average of V_0 from the four torsional frequencies ν_t given above). In the related molecules $C(CH_3)_4$ and $N(CH_3)_3$ the barrier V_0 has been estimated[318] as 4200 and 4270 cm^{-1}, respectively. It is therefore concluded that at 298.15 K ($k_BT/hc \sim 200$ cm^{-1}) the entropy value for the "rigid" configuration is applicable.

The values of $S_i°(g)$ reported previously for this ion are 417.1 J K^{-1} mol^{-1} by Boyd (1969)[312] (obtained after subtraction of the translational entropy contributions of the anions from the values reported for the ion pairs with the halide anions), and 308 J K^{-1} mol^{-1} by Johnson (1973).[319] The reason for this large discrepancy is unclear, since the input data on the basis of which these values have been calculated have not been stated explicitly. If it is presumed that T_d symmetry (and free CH_3 rotation) has been assumed by Johnson;[319] hence a term R ln 12 subtracted in his S_{rot} term, the correction of 20.7 J K^{-1} mol^{-1} brings his value to 329 J K^{-1} mol^{-1}, within 3 J K^{-1} mol^{-1} of the present value given above.

115a. Tetraethylammonium, $(C_2H_5)_4N^+$, and Tetratrapropylammonium, $(C_3H_7)_4N^+$. Johnson (1973)[319] reported $S_i°(g)$ = 462 and 620 J K^{-1} mol^{-1}, respectively, for these two ions, but did not give his input data. On the presumption that free rotation of the alkyl groups has been assumed, hence T_d symmetry prevails, and $-R$ ln 12 has been included in S_{rot}, the correction for hindered rotation brings these values up to 483 and 641 J K^{-1} mol^{-1}, respectively.

Registry No. OH^-, 14280-30-9; SH^-, 15035-72-0; SeH^-, 16661-43-1; TeH^-, 18282-39-8; O_2^-, 11062-77-4; O_2^{2-}, 14915-07-2; ClO^-, 14380-61-1; BrO^-, 14380-62-2; NO^+, 14452-93-8; VO^{2+}, 20644-97-7; CN^-, 57-12-5; S_2^{2-}, 16734-12-6; Hg_2^{2+}, 12596-26-8; N_3^-, 14343-69-2; S_3^{2-}, 12597-05-6; Br_3^-, 14522-80-6; I_3^-, 14900-04-0; HF_2^-, 18130-74-0; HO_2^-, 14691-59-9; BO_2^-, 14100-65-3; AlO_2^-, 20653-98-9; NO_2^+, 14522-82-8; NO_2^-, 14797-65-0; ClO_2^-, 14998-27-7; VO_2^+, 18252-79-4; BrO_2^-, 15477-77-7; UO_2^{2+}, 16637-16-4; NpO_2^{2+}, 18973-22-3; PuO_2^{2+}, 22853-00-5; AmO_2^{2+}, 12323-66-9; UO_2^+, 21294-41-7; NpO_2^+, 21057-99-8; PuO_2^+, 22967-56-2; AmO_2^+, 22878-02-0; NCO^-, 661-20-1; NCS^-, 302-04-5; $AgCl_2^-$, 15955-35-8; $AgBr_2^-$, 15930-33-3; AgI_2^-, 18444-29-6; OH_3^+, 13968-08-6; ClO_3^-, 14866-68-3; BrO_3^-, 15541-45-4; IO_3^-, 15454-31-6; SO_3^{2-}, 14265-45-3; SeO_3^{2-}, 14124-67-5; TeO_3^{2-}, 15852-22-9; NO_3^-, 14797-55-8; CO_3^{2-}, 3812-32-6; VO_3^-, 13981-20-9; HCO_2^-, 71-47-6; $N_2O_2^{2-}$, 15435-66-2; BrO_4^-, 16474-32-1; TcO_4^-, 14333-20-1; TeO_4^{2-}, 15845-23-5; MnO_4^{2-}, 14333-14-3; SbO_4^{3-}, 20175-28-4; VO_4^{3-}, 14333-18-7; ClO_4^-, 14797-73-0; IO_4^-, 15056-35-6; MnO_4^-, 14333-13-2; ReO_4^-, 14333-24-5; SO_4^{2-}, 14808-79-8; SeO_4^{2-}, 14124-68-6; CrO_4^{2-}, 13907-45-4; MoO_4^{2-}, 14259-85-9; WO_4^{2-}, 14311-52-5; PO_4^{3-}, 14265-44-2; AsO_4^{3-}, 15584-04-0; SiO_4^{4-}, 17181-37-2; NH_4^+, 14798-03-9; PH_4^+, 16749-13-6; BH_4^-, 16971-29-2; AlH_4^-, 19469-81-9; BF_4^-, 14874-70-5; $B(OH)_4^-$, 15390-83-7; $Al(OH)_4^-$, 14485-39-3; HSO_3^-, 15181-46-1; FSO_3^-, 15181-47-2; $S_2O_3^{2-}$, 14383-50-7; HCO_3^-, 71-52-3; $HSeO_3^-$, 20638-10-2; $Ag(CN)_2^-$, 15391-88-5; $Au(CN)_2^-$, 14950-87-9; $AuCl_4^-$, 14337-12-3; $Pd(NH_3)_4^{2+}$, 15974-14-8; $Pt(NH_3)_4^{2+}$, 16455-68-8; HSO_4^-, 14996-02-2; $HSeO_4^-$, 14998-57-3; $HCrO_4^-$, 15596-54-0; HPO_4^{2-}, 14066-19-4; $H_2PO_4^-$, 14066-20-7; $HAsO_4^{2-}$, 16844-87-4; $H_2AsO_4^-$, 16518-47-1; HVO_4^{2-}, 26450-38-4; $H_2VO_4^-$, 34786-97-5; $C_2O_4^{2-}$, 338-70-5; $S_2O_4^{2-}$, 14844-07-6; $S_2O_5^{2-}$, 23134-05-6; $S_2O_6^{2-}$, 14781-81-8; $S_2O_7^{2-}$, 16057-15-1; $S_2O_8^{2-}$, 15092-81-6; $S_4O_6^{2-}$, 15536-54-6; $P_2O_6^{4-}$, 16566-52-2; $P_2O_7^{4-}$, 14000-31-8; $Cr_2O_7^{2-}$, 13907-47-6; $N_2H_5^+$, 62901-69-3; $N_2H_6^{2+}$, 24778-64-1; AlF_6^{3-}, 21340-03-4; SiF_6^{2-}, 17084-08-1; SnF_6^{2-}, 21340-04-5; $RhCl_6^{3-}$, 21412-00-0; $PdCl_6^{2-}$, 17141-41-2; $SnCl_6^{2-}$, 16871-48-0; $ReCl_6^{2-}$, 16871-50-4; $IrCl_6^{3-}$, 14648-50-1; $IrCl_6^{2-}$, 16918-91-5; $PtCl_6^{2-}$, 16871-54-8; $SnBr_6^{2-}$, 16871-49-1; $Co(CN)_6^{3-}$, 14897-04-2; $Fe(CN)_6^{3-}$, 13408-62-3; $Fe(CN)_6^{4-}$, 13408-63-4; $Co(NH_3)_6^{3+}$, 14695-95-5; $CH_3CO_2^-$, 71-50-1; $CF_3CO_2^-$, 14477-72-6; NH_3OH^+, 43332-84-9; $CH_3NH_3^+$, 17000-00-9; $(CH_3)_4N^+$, 51-92-3; $(C_2H_5)_4N^+$, 66-40-0; $(C_3H_7)_4N^+$, 13010-31-6; $ClSO_3^-$, 15181-48-3.

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