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Improvements in Estimated Entropies and Related Thermodynamic Data for Aqueous Metal Ions

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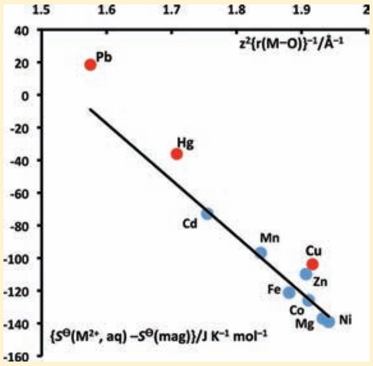
ABSTRACT: New estimated standard entropies for some aqueous metal ions are obtained by taking account of magnetic and symmetry contributions. By combining them with an analysis of literature data, improved experimental and estimated values are derived for the standard enthalpies and Gibbs energies of formation of the aqueous ions of titanium, vanadium, chromium, manganese, cerium, and praseodymium. Separate entropy correlations are used for each primary coordination number, and the size dependence is represented by the reciprocal of the metal−oxygen distance in that coordination. The new scheme is consistent with recent work on the coordination of Hg^{2+}(aq), Pb^{2+}(aq), and tripositive rare earth ions. It differs from its predecessors in indicating a larger variation of the standard molar entropies of aqueous ions with coordination number. The value of $S^\ominus(Be^{2+}, aq)$ is discussed in this context.



■ INTRODUCTION

The determination of standard entropies of the more highly charged aqueous ions is quite difficult, and the uncertainties in experimental values are often large. For this reason, empirical equations for estimating such entropies have a particular importance. Although some authors still use the older Powell−Latimer equation,[1] most now give preference to the equations developed in papers by Shock and co-workers.[2−4] We adopt this preference here.

Experimental values of the standard entropies of aqueous ions are tabulated at 25 °C using a convention upon which $S^\ominus(H^+,aq) = 0$. In Shock and Helgeson's estimation scheme,[2] such values for positive monatomic ions were fitted to an expression of the form:

$$S^\ominus = \{-Mz^2/(r_p + \beta z)\} + \alpha z \tag{1}$$

Here, z is the charge number of the ion, and M, α, and β are constants with the values 458.8 Å J K^{-1} mol^{-1}, 299.2 J K^{-1} mol^{-1}, and 0.940 Å, respectively. The size parameter r_p is the Pauling crystal radius in six-coordination.

In a further paper, Sassani and Shock[3] refined this procedure by trying to allow for the variation in $S^\ominus$ with the coordination number of the aqueous ion. Separate equations were generated for the different possible coordination numbers, and Pauling's crystal radius, r_p, was replaced by the Shannon radius, r_s,[5] for the coordination number in question. Sassani and Shock's scheme is therefore represented by the generic equation:

$$S^\ominus = \{-Mz^2/(r_s + \beta z)\} + \alpha z \tag{2}$$

The daughter equations for the different coordination numbers are generated by using different tabulated values for M and α.

These schemes are impressive because of their comprehensive nature: they succeed in correlating the entropies of many aqueous ions in spite of large variations in charge, size, and coordination number. In this paper, however, we begin with a very restricted range of ions: dipositive and tripositive ions for which there is strong evidence of a coordination number of six in aqueous solution. The ions in question are listed in Table 1, and for reasons that will become apparent, the tripositive ions appear first. The coordination geometry for all of these ions is octahedral or distorted octahedral. Strong evidence of this is provided by X-ray and spectroscopic studies of both solid compounds and aqueous solutions.[6−14] We thus obtain two series within which there is a high probability that both the charge and the coordination number are fixed. Equation 2 then implies that in each series, $S^\ominus$ varies linearly with $1/(r_s + \beta z)$, βz being a constant.

Restricting the possible variables in this way has two advantages. First, it allows us to estimate with greater confidence the unknown entropies of other ions that also share the common properties of the sets. Second, it makes it easier to identify the source of any irregularities in the linear correlations and therefore to suggest refinements. That a search for refinements might be worthwhile is apparent from the first entry in Table 2. This shows the R^2 values of Sassani and Shock's linear correlations for our two series. All of the data

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Table 1. Properties of Six-Coordinate Ions in Aqueous Solution

	r(M−O), Å	r_s, Å	r_s', Å	$S^\ominus$, J K^{-1} mol^{-1}	ground state	$S^\ominus$(mag), J K^{-1} mol^{-1}	$S^\ominus(\sigma)$, J K^{-1} mol^{-1}	$S^\ominus$(corr), J K^{-1} mol^{-1}
Co^{3+}	1.873	0.545	0.542	−348 ± 25[b]	$^1A_{1g}$	0	0	−348
Al^{3+}	1.877	0.535	0.546	−346 ± 15[d]	$^1S_0$	0	0	−346
Ga^{3+}	1.944	0.620	0.613	−317 ± 25[b]	$^1S_0$	0	0	−317
Fe^{3+}	1.995	0.645	0.664	−278 ± 8[c]	$^6A_{1g}$	14.9	0	−293
In^{3+}	2.112	0.800	0.781	−264 ± 25[b]	$^1S_0$	0	0	−264
Tl^{3+}	2.232	0.885	0.901	−217 ± 25[b]	$^1S_0$	0	0	−217
Ni^{2+}	2.060	0.690	0.710	−130.0 ± 2[b]	$^3A_{2g}$	9.1	0	−139
Mg^{2+}	2.069	0.720	0.719	−137 ± 4[a]	$^1S_0$	0	0	−137
Zn^{2+}	2.097	0.740	0.747	−109.8 ± 1.5[a]	$^1S_0$	0	0	−109.8
Cu^{2+}	2.087	0.730	0.737	−98 ± 4[a]	$^2B_{1g}$	5.8	9.1	−113
Co^{2+}	2.093	0.745	0.743	−111 ± 5[b]	$^4T_{1g}$	15.2	0	−126
Fe^{2+}	2.126	0.780	0.776	−101.6 ± 4[c]	$^5T_{2g}$	19.6	0	−121
Mn^{2+}	2.178	0.830	0.828	−82 ± 7[b]	$^6A_{1g}$	14.9	0	−97
Cd^{2+}	2.279	0.950	0.929	−72.8 ± 1.5[a]	$^1S_0$	0	0	−72.8
Hg^{2+}	2.342	1.020	0.992	−36.2 ± 0.8[a]	$^1S_0$	0	20.7	−56.9
Pb^{2+}	2.54	1.190	1.190	+18.5 ± 1[a]	$^1S_0$	0	20.7	−2.2

[a]Reference 20. [b]See Appendix 1. [c]Parker, V. B.; Khodakovskii, I. L. *J. Phys. Chem. Ref. Data*, **1995**, *24*, 1699. [d]The value obtained from the solubility of gibbsite and recommended by Bénézeth, P.; Palmer, D. A.; Wesolowski, D. J. *Geochim. Cosmochim. Acta* **2001**, *65*, 2097.

Table 2. Progressive Refinement of Linear Correlations Used to Estimate the Entropies of Aqueous Ions in Table 1

	R^2	
estimation scheme	tripositive ions	dipositive ions
1. References 3 and 4	0.816	0.927
2. As 1 with updated data and r_s'	0.964	0.953
3. As 2 but corrected for $S^\ominus$(mag)	0.993	0.958
4. As 3 but corrected for $S^\ominus(\sigma)$	(0.993)	0.971
5. As 4 using $[r(\text{M−O})]^{-1}$ dependence	0.993	0.970

were taken from references 3 and 4 except for $r_s(Co^{3+})$. Reference 3 took the high-spin value, but as Co^{3+} is low-spin,[15] we have used Shannon's value of 0.545 Å for this state. Both R^2 values reveal strong correlations, but there is clearly room for improvement, especially in the case of the tripositive ions where R^2 = 0.816.

In an attempt to improve the correlations, we shall start with the raw data. Most of the experimental entropies used in references 2 and 3 were taken from the NBS compilation,[16] which is based upon reviews completed in the 1960s and 1970s. We have therefore tried to improve some of the values by reassessing them and using more recent work. We shall also recalibrate the Shannon radii[5] by making them consistent with the observed metal−oxygen distances in solid compounds containing the complexes $[M(H_2O)_6]^{n+}$. Following these adjustments, we shall review the correlations and look for possible refinements.

■ KEY DATA

Internuclear Distances and Ionic Radii. The metal−oxygen distances in the relevant $[M(H_2O)_6]^{n+}$ complexes are shown in column 2 of Table 1. The values for the dipositive ions were taken from X-ray studies of the ammonium Tutton salts[10−13] and perchlorate hydrates,[17,18] those for the tripositive ions from cesium alums[14] and thallium perchlorate hexahydrate.[19] Column 3 contains the shorter Shannon ionic radii, r_s, used by Sassani and Shock.[3,4] These were recalibrated by

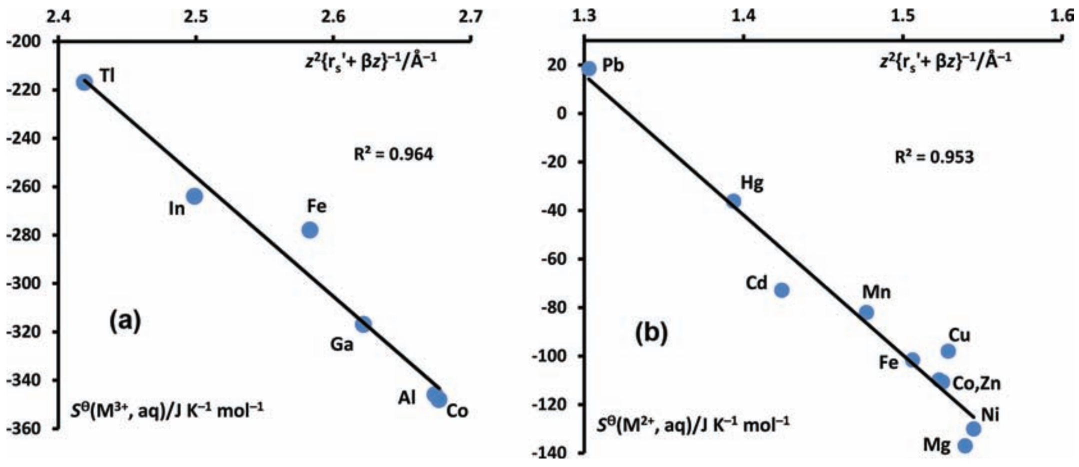

Figure 1. Revised and updated standard molar entropies plotted against $z^2/(r_s + \beta z)$ where the values of r_s have been recalibrated using the mean metal−oxygen internuclear distances in the hexa-aqua complexes: (a) six-coordinated aqueous tripositive ions (βz = 2.82 Å); (b) six-coordinated aqueous dipositive ions (βz = 1.88 Å).

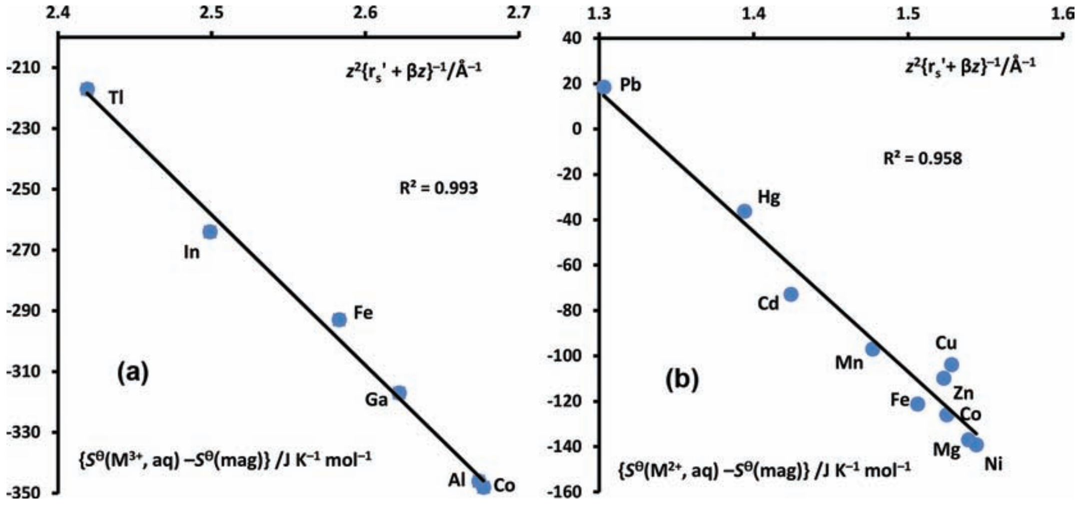

Figure 2. The result of subtracting, where appropriate, a magnetic contribution from the entropies of Figure 1: (a) six-coordinated aqueous tripositive ions; (b) six-coordinated aqueous dipositive ions.

subtracting the average difference between columns 2 and 3 from the internuclear distances in column 2, the calculation being performed separately for the dipositive and tripositive ions. The results are displayed in column 4 as revised ionic radii, r_s'.

Selected Standard Molar Entropies. Our values appear in column 5 of Table 1. They are consistent with *CODATA Key Values for Thermodynamics*,[20] and indeed, six of them have been taken from this source. Unless otherwise stated, any required auxiliary data unavailable in reference 20 were taken from reference 16. Our selections for seven of the ions merit further comment, and they are discussed in Appendix 1.

REFINEMENT OF THE CORRELATIONS

We shall now see if our revised entropies and recalibrated ionic radii improve the quality of Sassani and Shock's correlations. Figure 1 shows the result of repeating them with the new input data, and the second entry in Table 2 shows the revised R^2 values. Comparison with the first entry shows that the improvements are considerable, especially in the case of the tripositive ions. However, irregularities remain, and in seeking refinements that reduce them, we begin with the tripositive ions because in this case refinement is simpler. We shall then discuss the dipositive ions where there are additional complications. Finally, we shall test the ideas that have been elicited from these two exercises by trying to understand variations in the entropies of aqueous lanthanide ions.

Six-Coordinate Tripositive Ions. Figure 1a, with its revised input data, has increased the R^2 value from 0.816 to 0.964. However, one obvious irregularity remains: the entropy of Fe^{3+}(aq), the only one of the six ions with a nonsinglet ground state, lies well above the linear fit. A possible reason for this is magnetic entropy arising from ground state degeneracy plus a contribution from any accessible excited states. The possibility of including such a term in the estimation of the entropies of aqueous ions has been noted by Latimer and others.[1,21,22] But except in the case of the lanthanides, to which we return later, it is usually omitted from any correlations.

In the case of Fe^{3+}, the ground state is $^6A_{1g}$ and the magnetic entropy is $R \ln (2S + 1)$ or $R \ln 6 = 14.9$ J K^{-1} mol^{-1}. In column 9 of Table 1, this figure has been subtracted from $S^\ominus(Fe^{3+}, aq)$ and, in Figure 2a, Figure 1a has been replotted with that adjustment. R^2 has increased from 0.964 to 0.993. This strongly supports incorporation of magnetic contributions into methods of estimating the entropies of aqueous ions.

Six-Coordinate Dipositive Ions. We first repeat the operation we performed on $S^\ominus(Fe^{3+}, aq)$ by subtracting a magnetic contribution, $S^\ominus$(mag), from the values of $S^\ominus(M^{2+}, aq)$. The ground states of the hexa-aqua ions, prior to consideration of spin−orbit coupling, are shown in column 6 of Table 1. For the magnetic ions, the assumed symmetry of the ligand field is O_h except for Cu^{2+} where it is D_{4h}. For A and B ground states, the magnetic entropy is simply $R \ln(2S + 1)$. In the case of the T ground states of Fe^{2+} and Co^{2+}, the degeneracy is lifted by spin−orbit coupling, which generates three levels, all of which are accessible at room temperature. We have previously used the splitting pattern to calculate the energy of the complexes with respect to the barycenter of the three levels.[23−25] Here, we use it to calculate the magnetic entropy, the coupling parameters being $\lambda = 84$ cm^{-1} and $\lambda = 136$ cm^{-1}, respectively. The resulting values of $S^\ominus$(mag) are shown in column 7 of Table 1. Figure 2b shows the result of replotting Figure 1b after $S^\ominus$(mag) has been subtracted from $S^\ominus(M^{2+}, aq)$. Again, there is an improvement: R^2 increases from 0.953 to 0.958.

In the case of the dipositive ions, the improvement brought about by subtraction of a magnetic contribution is modest. However, Figure 2b is suggestive. Of the four ions whose entropies lie above the linear fit, three (Cu^{2+}, Hg^{2+}, and Pb^{2+}) do not have regular octahedral coordination. Their degree of separation from the other ions in Figure 2b, although clearly visible, is masked by the comprehensive regression. It is displayed more clearly by removing the three ions from the linear fit and marking their points in red. This has been done in Figure 3. They then lie above the line by some 20 J K^{-1} mol^{-1}. We suggest that this displacement can be explained by using symmetry arguments.

Such arguments require the assignment of a symmetry number, σ. The symmetry number is the number of independent permutations of identical atoms (or groups) that can be arrived at by simple rigid rotations of the entire complex. It can be obtained from the point group character table by adding one to the total number of simple rotational operations. In first row transition metal complexes, a strong Jahn−Teller

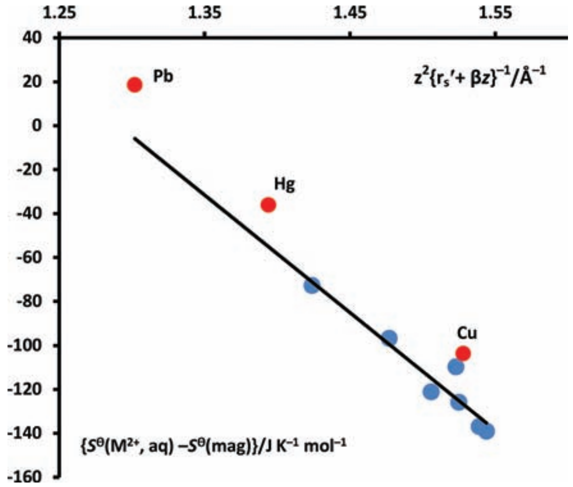

Figure 3. The result of replotting Figure 2b after removing the lead, mercury, and copper points from the linear fit and coloring them red.

effect acts upon the ions with d^4 and d^9 configurations and reduces the symmetry of the complex below O_h. This applies to Cu^{2+}. Although there is not total agreement about the situation in solution, the symmetry in the solid state is D_{4h}. The symmetry number, σ, is then 8 rather than 24. At d^4 and d^9, therefore, this type of distortion should increase the entropy of the ions, relative to those with O_h symmetry, by $R\ln(24/8) = R\ln 3$.

Recent work suggests that the octahedra around aqueous Hg^{2+} and Pb^{2+} are also strongly distorted, in the first case, by second order Jahn−Teller effects and, in the second, by the stereochemical influence of a hemidirected lone pair which reduces the symmetry number to two.[17,18] In the absence of more precise information about the distortions, we take $\sigma = 2$ in both cases. Here, then, the correction, $S^\ominus(\sigma)$, is $R\ln(24/2) = 20.7$ J K^{-1} mol^{-1}. The values of $S^\ominus(\sigma)$ for the complete set of ions appear in column 8 of Table 1.

Column 9 of Table 1 shows a corrected entropy, $S^\ominus$(corr), where

$$S^\ominus(\mathrm{corr}) = S^\ominus - S^\ominus(\mathrm{mag}) - R\ln(24/\sigma) \tag{3}$$

When $S^\ominus$(corr) rather than $\{S^\ominus - S^\ominus(\mathrm{mag})\}$ is plotted against $(r_s' + \beta z)^{-1}$, the linearity shown in Figure 2b is improved from $R^2 = 0.958$ to $R^2 = 0.971$.

This completes our refinement of Sassani and Shock's work in the case of the dipositive ions. For the tripositive ions in Table 1, the values of $S^\ominus(\sigma)$ are zero, so Figure 2a, with its R^2 value, represents an analogous completion for tripositive ions. However, we found that if the distance parameter $(r_s' + \beta z)$ is simply replaced by the metal−oxygen distance r(M−O) shown in column 2 of Table 1, the effects on R^2 are negligible in both cases. The two plots obtained in this way are shown in Figure 4. Because we shall use these correlations in later arguments, the plots include the equations that connect the two variables.

The Correlations and Experimental Uncertainties. The improvements brought about by the successive refinements that we propose are summarized by the R^2 values shown in Table 2. They are obvious, but when judging the quality of the correlations one must also take account of the experimental uncertainties in the data from which they were derived. Throughout this paper, the stated uncertainties represent confidence intervals of about 95%. For the dipositive ions of Figure 4b, deviations from the linear correlations exceed the experimental uncertainties, the largest being 12 J K^{-1} mol^{-1}. Accordingly, estimates obtained with the correlation have this level of uncertainty.

In the case of the tripositive ions in Figure 4a, the experimental uncertainties are very large, and the correlation is better than these might suggest. Support for the correlation is, however, provided by the dipositive ions. Nevertheless, estimates of the entropies of tripositive ions made using Figure 4a necessarily have the large uncertainties of the experimental values.

Tripositive Lanthanide Ions. We now consider the entropies of tripositive aqueous lanthanide ions, together with those of yttrium and lutetium. How the water molecules around these ions are coordinated is a longstanding problem. A recent investigation established analogies between the coordination in

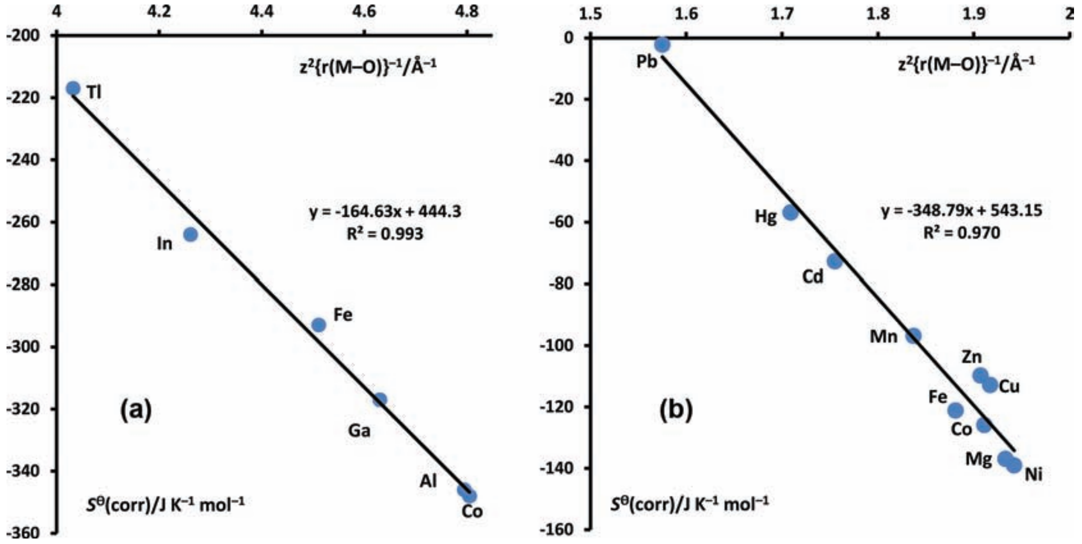

Figure 4. The result of subtracting a symmetry contribution, $R\ln(24/\sigma)$ from the entropies of Figure 2 and plotting the results against the reciprocal of the mean metal−oxygen distance in the hexa-aqua complexes: (a) six-coordinated aqueous tripositive ions; (b) six-coordinated aqueous dipositive ions.

aqueous solution and in the solid salts $[Ln(H_2O)_n](CF_3SO_3)_3$ by using EXAFS, XANES, and X-ray crystallography.[26,27] It was concluded that the coordination is based upon a trigonal, tricapped prism (TTP), but important changes occur across the series. In the solid trifluoromethane sulphonates, $n = 9$ in the lanthanum–neodymium region and all nine coordination sites are occupied by water molecules, with equal Ln–O bond lengths for the six prismatic ligands and somewhat longer but, again, equal bond lengths for the three capping positions. At samarium, the capping bond lengths become unequal, two of them becoming increasingly longer than the third as one moves further across the series. Toward the end of the series, a water molecule is lost from some of the two weakly bound capping positions generating some metal sites in an eight coordinate bicapped trigonal prism with unequal capping bond lengths. This change is marked by a fall in n. The deficiency in n is very small at holmium and erbium where $n > 8.9$ but becomes significant at thulium, ytterbium, and lutetium when $n = 8.8$, 8.7, and 8.4, respectively. The evidence from XANES and EXAFS also suggested that the cross-series changes in the coordination of the lanthanides in aqueous solution are very similar to those just described for the trifluoromethane sulphonates.

This argument implies that, in aqueous solution, the first dozen lanthanide elements have nine-coordinate TTP coordination with a distortion appearing in the region of samarium. However, at thulium, ytterbium, and lutetium, the solutions contain a significant proportion of unsymmetrical eight-coordinate tripositive ions. Now, in contrast to the trifluoromethane sulphonates, the solid ethylsulphates, $[Ln(H_2O)_9](C_2H_5OSO_3)_3$, do not develop water-deficiency as one moves across the series, and it appears that $n = 9$ throughout.[27,28] So from our earlier study of transition elements, we would expect that if, in aqueous solution, the tripositive ions of the lanthanides, yttrium, and lutetium were nine-coordinate and undistorted, then if the entropies were corrected for the presence of a magnetic contribution and plotted against the reciprocal of the average metal–oxygen distance in the ethylsulphates,[27−29] a straight line should be the result. On the other hand, if there is a drop in coordination number across the series or a change in symmetry number, there should be a break in the straight line.

The experimental values of the entropies[30,31] are shown in column 2 of Table 3. The uncertainties assessed by Spedding et al.[32] have been doubled, and we have included data on yttrium. Column 3 shows the magnetic entropies which were also calculated by Spedding et al.[32] Except at samarium and europium, these are equal to $R \ln(2J + 1)$ where $2J + 1$ is the degeneracy of the ground state. At samarium and europium, there are small additional contributions from excited states that are accessible at 298.15 K. Column 4 shows the values of $\{S^\ominus - S^\ominus(\text{mag})\}$ and column 5, the average metal–oxygen distances in the ethylsulphates.

To demonstrate the importance of correcting for the magnetic entropy, we first plot the uncorrected entropies against $9/r(\text{M–O})$ in Figure 5a. Linearity is poor ($R^2 = 0.696$), and the values for the nonmagnetic ions of lanthanum, yttrium, and lutetium are displaced downward with respect to the rest. The corrected entropies of Figure 5b show greatly improved linearity ($R^2 = 0.923$), and there is now little or no distinction between the magnetic and nonmagnetic ions. There is however a noticeable break between neodymium and samarium which would be diminished if the downward displacement of the lanthanum and neodymium points in Figure 5b were reduced or eliminated. This suggests an interpretation of the entropy values based upon the coordination changes that we have just discussed. Beyond neodymium, the capping bond lengths become unequal, and this destroys all of the D_{3h} symmetry of the complex, giving $\sigma = 1$. For the trigonal tricapped prism, $\sigma = 6$, and in Figure 5c, we show the results of subtracting $R \ln(6/1)$ from the trans-neodymium values. The same adjustment has been made to the yttrium value on the grounds of ionic size. The looked-for improvement in linearity is obtained ($R^2 = 0.973$).

Table 3. Data for Tripositive Aqueous Lanthanide Ions

ion	$S^\ominus$, J K^{-1} mol^{-1}	$S^\ominus$(mag), J K^{-1} mol^{-1}	$S^\ominus - S^\ominus$(mag), J K^{-1} mol^{-1}	r(M–O), Å
La^{3+}	−209 ± 4	0	−209	2.550
Ce^{3+}		14.9		2.527
Pr^{3+}		18.3		2.509
Nd^{3+}	−206 ± 4	19.2	−225	2.495
Sm^{3+}	−207 ± 6	15.1	−222	2.470
Eu^{3+}	−216 ± 4	9.2	−225	2.458
Gd^{3+}	−219 ± 4	17.2	−236	2.446
Tb^{3+}	−224 ± 4	21.3	−245	2.430
Dy^{3+}	−229 ± 4	23.0	−252	2.420
Ho^{3+}	−229 ± 4	23.4	−252	2.412
Er^{3+}	−235 ± 4	23	−258	2.409
Tm^{3+}	−236 ± 4	21.3	−257	2.395
Yb^{3+}	−241 ± 4	17.2	−258	2.386
Lu^{3+}	−264 ± 4	0	−264	2.378
Y^{3+}	−249 ± 6	0	−249	2.418

Our analysis is therefore remarkably consistent with the arguments of reference 26 and with the observations made in references 26 and 27, but it is not decisive. It could be modified to support other views[33,34] that favor a shift in coordination from nine-coordinate TTP to eight-coordinate square prismatic toward the end of the first half of the lanthanide series. In this case, the La–Nd downward displacement of some 15 J K^{-1} mol^{-1} would indicate a positive value of $\Delta S^\ominus$ for the process:

$$[M(H_2O)_9]^{3+}(aq) = [M(H_2O)_8]^{3+}(aq) + H_2O(l) \qquad (4)$$

Here, the symmetry numbers of 6 and 8 for the two ions are so similar that there is a negligible contribution from this source, and a positive value of $\Delta S^\ominus$ would be expected because of the increase in the number of particles. Values of $\Delta S^\ominus$ for reactions such as 4 are hard to determine. This is why the chosen standard state of an aqueous ion written $M^{n+}(aq)$ is an ideal solution of unit molality m, where m is the *total combined molality* of all hydrates in the solution.[35,36] However, a value of +25 J K^{-1} mol^{-1} for reaction 4 has been determined in the case of $Cm^{3+}(aq)$.[37]

This analysis suggests a further refinement to the first one. In Figure 5c, the three points at the end of the series all lie above the linear fit. If these are omitted from the regression procedure, the value of R^2 increases slightly to 0.976 despite the use of fewer points. The vertical displacements of the three terminal points from the new line are about 6 J K^{-1} mol^{-1}. Taken in conjunction with the average values of n suggested by the XANES and EXAFS studies, they suggest a value of about 15–20 J K^{-1} mol^{-1} for $\Delta S^\ominus$ of reaction 4.

However, Figure 5 shows that, whatever conclusions are drawn about coordination change in aqueous solutions of the lanthanide ions, the effect of this upon the entropies is

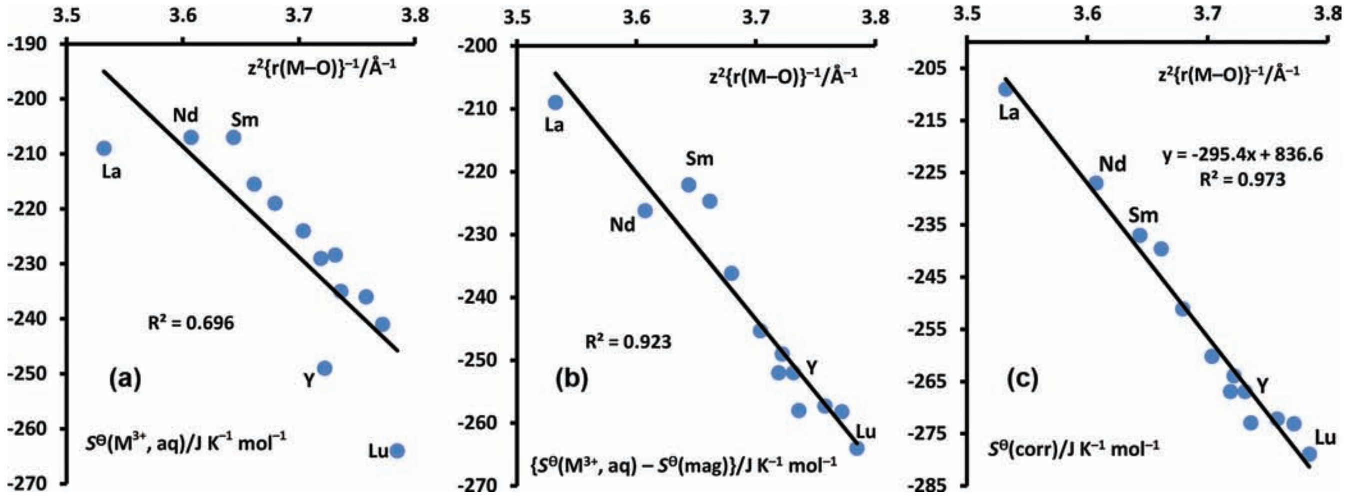

Figure 5. Entropies of aqueous lanthanide, yttrium, and lutetium ions plotted against $z^2\{r(\mathrm{M–O})\}^{-1}$ where $r(\mathrm{M–O})$ is the mean metal–oxygen[27−29] distance in the ethylsulphate hydrates, $[\mathrm{M(H_2O)_9}](\mathrm{C_2H_5OSO_3})_3$: (a) standard molar entropies; (b) as in part a but after subtraction of the magnetic entropies; (c) as in part b but with a symmetry factor R ln(6/1) subtracted for the trans-neodymium elements and yttrium.

Table 4. Revised Thermodynamic Data Suggested by This Work (columns 3-5) Compared with Previous Literature Data (columns 6 and 7)[a]

		this work			literature data	
substance	r(M–O), Å	$\Delta H_f^\ominus$, kJ mol^{-1}	$\Delta G_f^\ominus$, kJ mol^{-1}	$S^\ominus$, J K^{-1} mol^{-1}	$S^\ominus$, J K^{-1} mol^{-1}	$\Delta H_f^\ominus$, kJ mol^{-1}
Ce^{3+}(aq)	2.527	−702.4 ± 2	(−679 ± 3)	(−201 ± 7)	(−200)[30]	−700.4[30]
Pr^{3+}(aq)	2.509	−705.7 ± 2	(−681 ± 3)	(−205 ± 7)	(−194)[30]	−706.2[30]
Mn^{2+}(aq)		−221.9 ± 1	−226.8 ± 2	−82 ± 8	−73.6[16]	−220.8[16]
Mn^{3+}(aq)	1.991	(−106 ± 9)	−72 ± 3	(−277 ± 25)	(−310)[4]	
Cr^{2+}(aq)	2.167	−144.0 ± 3	(−153 ± 5)	(−78 ± 12)	(−46)[42]	−143.5[42]
Cr^{3+}(aq)	1.959	−230 ± 5	(−191 ± 9)	(−301 ± 25)	(−322)[4,42]	−243[42]
VO_2^+(aq)		−653.3 ± 2	−590.6 ± 2	−42 ± 8	−41.0[56]	−649.8[56]
VO^{2+}(aq)		−490.9 ± 3	−449.9 ± 2	−137 ± 10	−134[56]	−487.0[56]
V^{3+}(aq)	1.992	(−279 ± 8)	−245.1 ± 3	(−282 ± 25)	−230[56]	−259[56]
V^{2+}(aq)	2.137	(−219 ± 5)	−220 ± 3	(−98 ± 12)	−130[56]	−226[56]
TiO^{2+}(aq)		−690 ± 8	(−647 ± 9)	(−142 ± 15)		
Ti^{3+}(aq)	2.028	(−446 ± 13)	(−414 ± 10)	(−273 ± 25)		
Ti^{2+} (aq)	(2.172)	(−238 ± 10)	(−244 ± 11)	(−81 ± 12)		

[a] Column 2 shows r(M–O) values that were used to estimate entropies. These estimates and other data that rely upon them are shown in parentheses.

secondary to that of the magnetic contribution. We discuss the influence of coordination changes further later in the paper.

■ PREDICTED ENTROPIES OF SOME AQUEOUS IONS

We now use the linear correlations of Figures 4 and 5 to estimate the entropies of some aqueous monatomic ions. We have chosen examples for which experimental values are either nonexistent or have large uncertainties. The lanthanides are considered first and then some relevant first row transition elements in reverse order of atomic number. Unless otherwise stated, metal–oxygen distances in the appropriate complex are taken from references 10, 11, 14, and 27.

The Lanthanides. Morss[30] noted that the experimental data needed to provide values of $S^\ominus(\mathrm{Ce^{3+}}, \mathrm{aq})$ and $S^\ominus(\mathrm{Pr^{3+}}, \mathrm{aq})$ were incomplete and cited estimates provided by Rard (−200 and −194 J K^{-1} mol^{-1} respectively). We use Figure 5c with magnetic entropies of R ln 6 and R ln 9 to obtain −201 and −205 J K^{-1} mol^{-1}. Our praseodymium figure is very close to that proposed by Spedding et al.,[32] and both estimates are 4 J K^{-1} mol^{-1} more positive than those cited by the NBS.[16] They lead to the thermodynamic properties listed in Table 4. The values of $\Delta H_f^\ominus(\mathrm{Ce^{3+}}, \mathrm{aq})$ and $\Delta H_f^\ominus(\mathrm{Pr^{3+}}, \mathrm{aq})$ are those of Cordfunke and Konings.[38]

Manganese. Our initial linear correlations with previous data[3,4] (entry 1 in Table 2) gave a positive displacement of the manganese point which exceeded the magnetic entropy. This led us to undertake a review of the experimental data. As noted in Appendix 1, the main problem is the value of $\Delta G_f^\ominus(\mathrm{Mn^{2+}}, \mathrm{aq})$. The key experimental data are $\Delta H_f^\ominus(\mathrm{MnO_2}, \mathrm{s})$[39] and $E^\ominus(\mathrm{MnO_2}|\mathrm{Mn^{2+}})$,[40] and we have tried to improve the situation by achieving comparability between the samples of MnO_2 that were used in the determination of these two quantities. Our revised experimental value is $S^\ominus(\mathrm{Mn^{2+}}, \mathrm{aq}) = -82 \pm 8$ J K^{-1} mol^{-1}, and it appears in Table 4 with the values of $\Delta G_f^\ominus(\mathrm{Mn^{2+}}, \mathrm{aq})$ and $\Delta H_f^\ominus(\mathrm{Mn^{2+}}, \mathrm{aq})$ from which it was derived. Data on Mn^{3+}(aq) were obtained from our estimated entropy using D_{4h} symmetry and $r(\mathrm{M–O}) = 1.991$ Å[14] together with the redox potential $E^\ominus(\mathrm{Mn^{3+}}|\mathrm{Mn^{2+}}) = 1.60$ V.[41]

Chromium. The thermochemistry of the aqueous ions of chromium is in an unsatisfactory state. Ball and Nordstrom[42] reviewed the subject thoroughly and expressed their doubts by noting that their selected value, $S^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq}) = -45.6$ J K^{-1} mol^{-1}, differed by over 50 J K^{-1} mol^{-1} from the figure estimated by Sassani and Shock[3,4] ($S^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq}) = -102$ J K^{-1} mol^{-1}). Here, we examine the problem by considering the reaction

$$\mathrm{Cr}^{2+}(\mathrm{aq}) + \mathrm{H}^{+}(\mathrm{aq}) = \mathrm{Cr}^{3+}(\mathrm{aq}) + 1/2\mathrm{H}_2(\mathrm{g}) \qquad (5)$$

There are two routes to the value of $\Delta H^\ominus$. We begin with the one which involves the separate evaluation of $\Delta H_f^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq})$ and $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq})$.

A crucial measurement is the heat of solution of $\mathrm{CrCl_2(s)}$ in water, conducted under nitrogen to avoid oxidation. Gregory and Burton[43] determined a value $\Delta H = -76.0$ kJ mol^{-1}, but the dissolution took place in 0.1 molar KCl. Nevertheless, their measurement is helpful because it is in reasonable agreement with the older value of Recoura,[44] who found $\Delta H = -77.8$ kJ mol^{-1}, at a temperature "at or near 18 C"[45] for the process:

$$\mathrm{CrCl_2(s)} = \mathrm{CrCl_2(aq, 550\ H_2O)} \qquad (6)$$

From data on the heat capacities of the solids $\mathrm{MnCl_2}$, $\mathrm{FeCl_2}$, $\mathrm{CoCl_2}$, and $\mathrm{NiCl_2}$ and their solutions,[46−48] we estimate $\Delta C_p = -305 \pm 30$ J K^{-1} mol^{-1} for reaction 6. Heat of dilution data on the same solids suggest a correction of -2.8 ± 1 kJ mol^{-1} for the change to infinite dilution. These estimates lead to a standard heat of solution of $\Delta H_{\mathrm{sol}}^\ominus = -82.7 \pm 3$ kJ mol^{-1}, which, in combination with $\Delta H_f^\ominus(\mathrm{CrCl_2, s})$,[49] yields $\Delta H_f^\ominus(\mathrm{CrCl_2, aq}) = -478.2 \pm 3$ kJ mol^{-1} and $\Delta H_f^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq}) = -144.0 \pm 3$ kJ mol^{-1} at 25 °C. This value is close to that selected by the NBS (-143.5 kJ mol^{-1}),[16] which used a similar route. However, Kirklin,[50] who had access to the NBS files, claimed that their published value of $\Delta H_f^\ominus(\mathrm{CrCl_2, aq}) = -477.8$ kJ mol^{-1} contained a transcription error and should have been -473.2 kJ mol^{-1}. But he also shows that the latter figure was obtained by simply coupling the value of $\Delta H_f^\ominus(\mathrm{CrCl_2, s})$ with Recoura's published heat of solution. If so, it is corrected for neither temperature nor dilution. We therefore persevere with the figure $\Delta H_f^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq}) = -144.0 \pm 3$ kJ mol^{-1} and turn to $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq})$.

After extensive consideration of published heats of reduction of chromium(VI) species to chromium(III), Ball and Nordstrom concluded that the work of Evans[51] was the only source that could provide a reliable value of $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq})$. Evans determined the heat of reduction of a diluted solution of potassium dichromate by $\mathrm{Fe}^{2+}(\mathrm{aq})$ in 0.5 M $\mathrm{HClO_4}$. He assumed that the species present in the diluted solution was $\mathrm{Cr_2O_7}^{2-}(\mathrm{aq})$. However, Ball and Nordstrom's selected data on $\mathrm{Cr_2O_7}^{2-}(\mathrm{aq})$, $\mathrm{HCrO_4}^{-}(\mathrm{aq})$, and $\mathrm{H_2CrO_4(aq)}$[42] suggest that most of the dissolved chromium is present as $\mathrm{HCrO_4}^{-}(\mathrm{aq})$ and only the residue as $\mathrm{Cr_2O_7}^{2-}(\mathrm{aq})$. By using a study, made in perchlorate media, of the variation of the equilibrium quotient with ionic strength,[52] we find that the composition was approximately 81% $\mathrm{HCrO_4}^{-}(\mathrm{aq})$ and 19% $\mathrm{Cr_2O_7}^{2-}(\mathrm{aq})$. Using these proportions with $\Delta H = 40.8$ kJ mol^{-1} for the enthalpy of oxidation of $\mathrm{Fe}^{2+}(\mathrm{aq})$ in 0.5 M $\mathrm{HClO_4}$,[53] we obtain $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq}) = -229.7$ kJ mol^{-1}; the value proposed by Ball and Nordstrom is some 10 kJ mol^{-1} more negative. Other determinations of enthalpies of reduction of chromium(VI) species that were rejected in reference 42 give values of $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq})$ in the range -230 to -238 kJ mol^{-1}. We therefore adopt the adjusted Evans value $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq}) = -229.7 \pm 5$ kJ mol^{-1}. With our $\Delta H_f^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq})$, it then yields $\Delta H^\ominus = -85.7 \pm 6$ kJ mol^{-1} for reaction 5.

Another value can be obtained from the enthalpy of oxidation of $\mathrm{Cr}^{2+}(\mathrm{aq})$ by $\mathrm{Fe}^{3+}(\mathrm{aq})$ in 0.5 M $\mathrm{HClO_4}$, and this[54] gives $\Delta H^\ominus(5) = -111.1$ kJ mol^{-1}. The discrepancy between the two values of $\Delta H^\ominus(5)$ can be expressed in terms of entropies. Ball and Nordstrom selected $E^\ominus(\mathrm{Cr}^{3+}|\mathrm{Cr}^{2+}) = -0.378 \pm 0.005$ V, which yields $\Delta G^\ominus(5) = -36.5 \pm 0.5$ kJ mol^{-1}. Thus, the enthalpy change based on the work of Evans gives $\Delta S^\ominus(5) = -165 \pm 20$ J K^{-1} mol^{-1}; that calculated from the chromium(II) oxidation leads to $\Delta S^\ominus(5) = -250$ J K^{-1} mol^{-1}. We can use our entropy estimation scheme to see which of these two very different values is to be preferred. For $\mathrm{Cr}^{2+}(\mathrm{aq})$, the assumed symmetry is D_{4h} with $\sigma = 8$; for $\mathrm{Cr}^{3+}(\mathrm{aq})$, it is O_h with $\sigma = 24$. The required estimates appear in Table 4. We find $\Delta S^\ominus(5) = -159$ J K^{-1} mol^{-1} and therefore select the value of $\Delta H_f^\ominus(\mathrm{Cr}^{3+}, \mathrm{aq})$ obtained from Evans's work. The thermodynamic properties obtained from this choice and our estimated entropies are shown in Table 4. Our estimated value $S^\ominus(\mathrm{Cr}^{2+}, \mathrm{aq}) = -78$ J K^{-1} mol^{-1} is different from that of Sassani and Shock (-102 J K^{-1} mol^{-1})[3,4] because the combined effects of magnetism and symmetry are large (23 J K^{-1} mol^{-1}).

The deviant value of $\Delta H^\ominus(5)$ derived from chromium(II) oxidation might be due to side reactions. Biedermann and Romano,[55] from whose data Ball and Nordstrom obtained their selected value of $E^\ominus(\mathrm{Cr}^{3+}|\mathrm{Cr}^{2+})$, worked in chloride solution. Their original plan to make measurements in perchlorate was thwarted by the occurrence of the reaction

$$\begin{aligned} &8\mathrm{Cr}^{2+}(\mathrm{aq}) + \mathrm{ClO_4}^{-}(\mathrm{aq}) + 8\mathrm{H}^{+}(\mathrm{aq}) \\ &\quad = 8\mathrm{Cr}^{3+}(\mathrm{aq}) + 4\mathrm{H_2O(l)} + \mathrm{Cl}^{-}(\mathrm{aq}) \end{aligned} \qquad (7)$$

They were also unable to prepare chloride-free solutions of chromium(II) perchlorate.

Vanadium. Our estimated entropies for $\mathrm{V}^{2+}(\mathrm{aq})$ and $\mathrm{V}^{3+}(\mathrm{aq})$ are shown in Table 4. In O_h symmetry, the ground states are $^4A_{2g}$ and $^3T_{1g}$. The magnetic entropy of $\mathrm{V}^{3+}(\mathrm{aq})$ was calculated using the values $\lambda = 85$ cm^{-1} and $A = 1.18$ obtained in previous work.[23,25] The result was 17.3 J K^{-1} mol^{-1}. For $\mathrm{V}^{2+}(\mathrm{aq})$, the magnetic entropy is simply $R \ln 4$.

Hill and co-workers reviewed vanadium thermochemistry.[56] We have updated their scheme for evaluating the properties of $\mathrm{VO_2}^{+}(\mathrm{aq})$ and $\mathrm{VO}^{2+}(\mathrm{aq})$ by making two modifications. First, we used more recent values of the enthalpy of formation[57] and entropy[58] of $\mathrm{V_2O_5}$. Second, as in other places, the EMF values for standard cells used in electrochemical measurements were calculated from the CODATA tables.[20] The results are shown in Table 4. From these data, we used $E^\ominus(\mathrm{VO}^{2+}|\mathrm{V}^{3+}) = 0.335$ V[59] and $E^\ominus(\mathrm{V}^{3+}|\mathrm{V}^{2+}) = -0.256$ V[60] to obtain $\Delta G_f^\ominus(\mathrm{V}^{3+}, \mathrm{aq})$ and $\Delta G_f^\ominus(\mathrm{V}^{2+}, \mathrm{aq})$. Our estimated entropies then provide $\Delta H_f^\ominus(\mathrm{V}^{3+}, \mathrm{aq})$ and $\Delta H_f^\ominus(\mathrm{V}^{2+}, \mathrm{aq})$.

Titanium. In O_h symmetry, the ground states of $[\mathrm{Ti(H_2O)_6}]^{2+}$ and $[\mathrm{Ti(H_2O)_6}]^{3+}$ are $^3T_{1g}$ and $^2T_{2g}$, respectively. The splitting brought about by spin−orbit coupling was estimated by using the values $\lambda = 49$ cm^{-1} and $A = 1.22$ for $\mathrm{Ti}^{2+}(\mathrm{aq})$ and $\lambda = 122$ cm^{-1} for $\mathrm{Ti}^{3+}(\mathrm{aq})$, obtained by the method of references 23 and 25. The same source provides the estimate $r(\mathrm{Ti{-}O}) = 2.172$ Å for the complex $[\mathrm{Ti(H_2O)_6}]^{2+}$. The estimated entropies of $\mathrm{Ti}^{2+}(\mathrm{aq})$ and $\mathrm{Ti}^{3+}(\mathrm{aq})$ are shown in Table 4, the calculated values of $S^\ominus(\mathrm{mag})$ being 17.9 and 12.9 J K^{-1} mol^{-1}, respectively.

We have previously combined very limited experimental data with estimated entropies to get approximate thermodynamic properties of the ions $\mathrm{TiO}^{2+}(\mathrm{aq})$, $\mathrm{Ti}^{3+}(\mathrm{aq})$, and $\mathrm{Ti}^{2+}(\mathrm{aq})$.[61]

Table 5. Estimating the Standard Entropy Change of Reaction 10[a]

	$S^\ominus$, J K^{-1} mol^{-1}	r_6(M–O), Å	$S_6^\ominus$ (Figure 4b), J K^{-1} mol^{-1}	$\Delta S^\ominus$, J K^{-1} mol^{-1}	$\Delta S^\ominus + R \ln 3$, J K^{-1} mol^{-1}	$\Delta S^\ominus + R \ln 24$, J K^{-1} mol^{-1}
Ca^{2+}(aq)	−56.2[b]	2.35	−50.4	6	15	32
Sr^{2+}(aq)	−31.5[c]	2.53	−8.4	23	32	50
Eu^{2+}(aq)	−10[d]	2.52	+6.7[e]	17	26	43
Ba^{2+}(aq)	8.8[c]	2.70	+26.1	17	26	44

[a] The subscript 6 in the headings of columns 3 and 4 specifies regular octahedral environments for the ions. [b] Reference 20. [c] Parker, V. B. *J. Phys. Chem. Ref. Data* **1995**, *24*, 1023. [d] Reference 30. [e] A magnetic entropy of $R \ln 8$ has been added.

Here, we repeat the calculation with our new estimates. The estimate $S^\ominus(TiO^{2+}, aq) = -142$ J K^{-1} mol^{-1} was obtained by removing a magnetic entropy $R \ln 2$ from the value for VO^{2+}(aq). The results appear in Table 4. From these data, the estimated value of $E^\ominus(Ti^{3+}|Ti^{2+})$ is −1.77 V, a figure which is about 1.0 V more negative than that obtained in recent quantum mechanical calculations.[62]

THE ENTROPIES OF AQUEOUS IONS AND COORDINATION NUMBER

Our scheme raises questions about the variation of the standard molar entropies of ions with coordination. This is a difficult problem, and one particular uncertainty should be mentioned at the outset. The standard state used for the entropies means that the coordination numbers required are those of the aqueous ion at infinite dilution. But the experimental X-ray techniques that are used to establish primary coordination numbers in solution (EXAFS, XANES and LAXS) are applied at typical concentrations of 0.5–4.0 M. Nevertheless, despite this gap between what experiment offers and theory requires, the preceding calculations suggest that the experimental coordination numbers provide useful insights into the entropy values.

The problem of the variation of the standard molar entropies with coordination was tackled by Sassani and Shock,[3,4] who produced separate empirical correlations for different coordination numbers. Their regression procedure seeks inverse correlations between the entropy of the ion and a distance parameter. But although the distance parameter is adjusted for change in coordination number, the *same value* of the entropy of the ion is used. For example, the same experimental value $S^\ominus(La^{3+}, aq) = -218$ J K^{-1} mol^{-1} appears in each of the linear correlations for six, seven, eight, nine, 10, and 12 coordination. It seems to us that such a procedure must produce results which understate the changes in the entropies of ions with coordination number. This is supported by the calculation of $S^\ominus(La^{3+}, aq)$ from the resulting Sassani–Shock equations for the six different coordination numbers just cited. The results lie in the range −189 to −198 J K^{-1} mol^{-1}. The experimentally observed value lies outside it because the correlations involve other ions. However, the important point is that the range is narrow, and there is no obvious trend in the variation with coordination number, the values for six and 12 coordination differing by only 2 J K^{-1} mol^{-1}. The experimental data for eight and nine coordinate curium[37] that we cited earlier are consistent with a larger variation, and our scheme supports this notion. Internuclear distances in crystals suggest that the ionic radii of In^{3+} and Lu^{3+} in the same coordination differ by 0.06 Å.[5] This implies that the metal–oxygen distance in $[Lu(H_2O)_6]^{3+}$ will be 2.17 Å, 0.06 Å longer than the value given for $[In(H_2O)_6]^{3+}$ in Table 1. Figure 4a then suggests that, in regular octahedral coordination, $S^\ominus(Lu^{3+}, aq) = -238$ J K^{-1} mol^{-1}, whence

$$Lu(H_2O)_n{}^{3+}(aq) = Lu(H_2O)_6{}^{3+}(aq) + (n-6)H_2O(l); \quad \Delta S^\ominus = 26\ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{8}$$

Here, n is thought to be eight or a combination of eight and nine (see above). The figures are very approximate, but as in the curium case, the value of $\Delta S^\ominus$ is positive. Furthermore, our calculation contains the in-built assumption that the $[Lu(H_2O)_6]^{3+}$ ion will be octahedral with a large symmetry number of 24. Relative to completely unsymmetrical ions, this lowers the entropy by 26 J K^{-1} mol^{-1}. If $\Delta S^\ominus(8)$ were corrected for this effect, the value (52 J K^{-1} mol^{-1} or 26 J K^{-1} per mole of water released) would be very close to the figure of 25 J K^{-1} per mole of water released that was observed in the curium reaction.

There are other indications that this figure has the right sign and magnitude. First, the entropy of melting of ice is 22 J K^{-1} mol^{-1}. This involves the release of water molecules from a fixed position into bulk water. Slightly greater values are obtained from the dehydration of hydrates that contain the complexes thought to exist in the aqueous ions, e.g.,

$$AlCl_3{\cdot}6H_2O(s) = AlCl_3(s) + 6H_2O(l); \quad \Delta S^\ominus = 212\ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{9}$$

Here, the value is about 35 J K^{-1} per mole of water.

An extension to the dipositive ions Ca^{2+}, Sr^{2+}, Eu^{2+}, and Ba^{2+} is less precise because the coordination is uncertain. Some studies point to an eight-coordinate square antiprismatic arrangement;[7,63] others favor more flexible and possibly asymmetric systems in which a range of coordination numbers between 7 and 11 occurs.[9,64–66] Nevertheless, all investigations agree that, with the possible exception of Ca^{2+}, the coordination numbers are greater than six. We can therefore write the observed ions of strontium, europium and barium as $[M(H_2O)_n]^{2+}$(aq) where $n > 6$. Then, when the effect of magnetism and symmetry numbers is removed, we expect distinctly positive values of $\Delta S^\ominus$ for the reaction:

$$M(H_2O)_n{}^{2+}(aq) = M(H_2O)_6{}^{2+}(aq) + (n-6)H_2O(l) \tag{10}$$

The calculations are summarized in the last three rows of Table 5. The estimated values of $S^\ominus(M^{2+}, aq)$ in regular octahedral coordination are shown in column 4. The metal–oxygen distances were estimated by adding the increment 1.35 Å deduced in Table 1 to the Shannon radii for six-coordination. Column 4 shows $S^\ominus$(corr) obtained from Figure 4b with the addition of a magnetic entropy of $R \ln 8$ in the case of Eu^{2+}(aq). Column 5 shows the estimated values of $\Delta S^\ominus(10)$. In column 6, we have made the symmetry correction for the studies which favor square antiprismatic coordination by adding $R \ln (24/8)$. In column 7, we repeat the exercise for studies which incline to a flexible asymmetric arrangement by adding $R \ln 24$. Columns 6 and 7 provide estimated lower and upper limits for the corrected values of $\Delta S^\ominus(10)$. All three ranges for the three larger ions cover distinctly positive values. The corrected entropy changes are roughly 15−20 J K^{-1} mol^{-1} per mole of water released. The value is lower than we encountered for the smaller and more highly charged ions, Cm^{3+}(aq) and Lu^{3+}(aq), but it is still substantial.

Table 5 also includes the calculations for calcium. Here, our estimated entropy in octahedral coordination is only 6 J K^{-1} mol^{-1} greater than the observed value. This is less than the potential error in our correlation, and it is therefore compatible with six-coordination. If however the hydration number is greater and the coordination less symmetrical as some workers claim,[63,64] the positive values in columns 6 and 7 are also consistent with this.

The extent of the variation of the entropies of ions with coordination is especially relevant to the value of $S^{\ominus}(Be^{2+}, aq)$. Past estimation schemes that take no account of coordination number[1,2] gave a value close to −230 J K^{-1} mol^{-1}. Sassani and Shock[3,4] used their correlation for four-coordinate ions to estimate −211 J K^{-1} mol^{-1}. However, Wagman et al.[16] quote an experimental value of −129.7 J K^{-1} mol^{-1}. This is less negative than the value for the six-coordinate Mg^{2+} (−137 J K^{-1} mol^{-1}), which has a larger ionic radius. We have checked Wagman's figure by combining the standard entropy,[67] heat of solution,[16] and solubility[68] of $BeSO_4{\cdot}4H_2O(s)$ with the osmotic and activity coefficients of $BeSO_4$(aq).[69,70] For the solution process, we find $\Delta G^{\ominus}$= 7.10 kJ mol^{-1} and $\Delta S^{\ominus}$ = −62.6 J K^{-1} mol^{-1}, which yields $S^{\ominus}(Be^{2+}, aq) = -128$ J K^{-1} mol^{-1}. Another route to the quantity gives an even more positive value. If the NBS heat of solution of $BeSO_4{\cdot}4H_2O$[16] is combined with a later standard enthalpy of formation,[71] we obtain $\Delta H_f^{\ominus}(Be^{2+},aq) = -378.5$ kJ mol^{-1}. Using $\Delta G_f^{\ominus}(Be^{2+},aq) = -381$ kJ mol^{-1} derived from measurements on beryllium hydroxides,[72] we find $S^{\ominus}(Be^{2+}, aq) = -116$ J K^{-1} mol^{-1}.

Now extrapolation of Figure 4b to a Be−O distance estimated using the Shannon radius for Be^{2+} in six-coordination[5] gives a value of $S^{\ominus}(Be^{2+}, aq)$ of about −230 J K^{-1} mol^{-1}. This is in good agreement with the other estimates we have mentioned, but it ignores the fact that the coordination number is lower than six and the effect that this will have. Comparison with the experimental value leads to an approximate entropy change for the interconversion of the two complex ions:

$$[Be(H_2O)_6]^{2+}(aq) = [Be(H_2O)_4]^{2+}(aq) + 2H_2O(l);$$
$$\Delta S^{\ominus} \sim 100\ J\ K^{-1}\ mol^{-1} \qquad (11)$$

The entropy change is about 50 J K^{-1} per mole of water released. This is much higher than the figure of 25 J K^{-1} obtained for Cm^{3+}, but the structural change is proportionately greater (6→4 instead of 9→8) and the beryllium ion is much smaller. The case of Be^{2+}(aq), therefore, seems to be a particularly marked instance of the influence of coordination number upon the entropies of ions.

CONCLUSION

Our estimation scheme differs from its predecessors in the attention paid to the primary coordination sphere of the ion. This allows us to separate out magnetic and symmetry contributions to the entropy that are independent of ion size. When these contributions have been removed, the size correlation is carried out with the residue. In making such correlations, previous workers have used an adjusted ionic crystal radius as the size parameter. Our view of the aqueous ion as part of a complex led us to look for an inverse correlation with the metal−oxygen distance, a quantity obtainable by experimental measurements upon the complex itself, either in the solid state or in solution.

We have applied the correlations separately to ions with the same charge and with a common coordination number for which there is strong experimental evidence. This requirement restricts the size of the data sets, but the results summarized in Table 2 and Figures 1−5 suggest that the modifications that we propose lead to improved correlations. At the same time, the estimated entropies that we have obtained for ions of manganese, chromium, and vanadium point to possible resolutions of uncertainties in the experimental thermochemistry of these elements. In the case of titanium, they provide tests of enthalpies of formation estimated by using ligand field theory.[25]

Finally, further application of the correlations led the work described in this paper toward a more general conclusion: the effect of change of coordination number upon the entropies of aqueous monatomic ions is more substantial than previous estimation schemes have either suggested or assumed.

APPENDIX 1

Auxiliary data, including $E^{\ominus}$ values for standard cells, have been taken from ref 20 or, if not available in that publication, from ref 16.

Manganese(II)

Three routes exist to the value of $\Delta H_f^{\ominus}(Mn^{2+},aq)$. First, by updating the value obtained from the heat of solution of manganese in acid,[73] we obtain $\Delta H_f^{\ominus}(Mn^{2+},aq) = -222.4$ kJ mol^{-1}. Secondly, Gedansky and Hepler's revision[74] of earlier work gives $\Delta H_f^{\ominus}(MnSO_4, s) = -1066.5$ kJ mol^{-1}. We have extrapolated heats of solution at high dilution[16,74] to infinite dilution using Pitzer's theory[75] and obtained $\Delta H^{\ominus}_{sol}(MnSO_4, s) = -64.6$ kJ mol^{-1}. This gives $\Delta H_f^{\ominus}(Mn^{2+},aq) = -221.8$ kJ mol^{-1}. A third route exploits the value[76] $\Delta H_f^{\ominus}(MnCl_2, s) = -481.95$ kJ mol^{-1}. Separate heat of dilution data[73,77] were combined and fitted to a Pitzer expression[75] for $^{\Phi}L$. Three values of the heat of solution at high dilution[78−80] then each give a value of $\Delta H_f^{\ominus}(Mn^{2+},aq)$. The average is $\Delta H_f^{\ominus}(Mn^{2+},aq) = -221.6$ kJ mol^{-1}. The average of this figure and the two values obtained by the other two routes gives $\Delta H_f^{\ominus}(Mn^{2+},aq) = -221.9 \pm 1$ kJ mol^{-1}.

Calculation of $\Delta G_f^{\ominus}(Mn^{2+},aq)$ begins with Shomate's value[39] of $\Delta H_f^{\ominus}(MnO_2, s)$. Updated evaluation of the two routes used by Shomate, including the incorporation of a recent value of $\Delta H_f^{\ominus}(MnO, s)$,[81] gives $\Delta H_f^{\ominus}(MnO_2, s) = -519.4 \pm 1$ kJ mol^{-1}. The entropies of the metal and the oxide[82] then yield $\Delta G_f^{\ominus}(MnO_2, s) = -464.4 \pm 1$ kJ mol^{-1}, and this can be combined with $E^{\ominus}(MnO_2|Mn^{2+})$ to give $\Delta G_f^{\ominus}(Mn^{2+},aq)$. However, attempts to determine $E^{\ominus}(MnO_2|Mn^{2+})$ give values[40] in the range 1.19−1.25 V depending upon the method by which the sample is prepared. Lower values seem to be associated with the most stoichiometric samples. The sample prepared for Shomate's experiments was very close to stoichiometric and, in this respect, and in the preparative method, corresponds closely to sample 2(ii) of ref 40. This gave $E^{\ominus}(MnO_2|Mn^{2+}) = 1.227$ V. We therefore accept this value, which yields $\Delta G_f^{\ominus}(Mn^{2+},aq) = -226.8 \pm 2$ kJ mol^{-1} and $S^{\ominus}(Mn^{2+}, aq) = -82 \pm 8$ J K^{-1} mol^{-1}.

Cobalt(II)

If the data of Haring and Westfall[83] are updated and combined with more recent activity coefficients,[69,70] we find $E^{\ominus}(\mathrm{Co^{2+}|Co}) = -0.287$ V and $\Delta G_f^{\ominus}(\mathrm{Co^{2+},aq}) = -54.4$ kJ mol^{-1}. There are two routes to $\Delta H_f^{\ominus}(\mathrm{Co^{2+},aq})$. Updating work and calculations[84] on $\mathrm{CoSO_4(s)}$ and its heat of solution, we find $\Delta H_f^{\ominus}(\mathrm{Co^{2+},aq}) = -58.5$ kJ mol^{-1}. Analogous work on $\mathrm{CoCl_2(s)}$[85,86] gives $\Delta H_f^{\ominus}(\mathrm{Co^{2+},aq}) = -59.0$ kJ mol^{-1}. We take the average, $\Delta H_f^{\ominus}(\mathrm{Co^{2+},aq}) = -58.8 \pm 0.6$ kJ mol^{-1}. With our value of $\Delta G_f^{\ominus}(\mathrm{Co^{2+},aq})$, this yields $S^{\ominus}(\mathrm{Co^{2+},\ aq}) = -112$ J K^{-1} mol^{-1}.

Heats of solution of $\mathrm{CoSO_4{\cdot}7H_2O(s)}$[87,88] can be extrapolated to infinite dilution using data on $\mathrm{NiSO_4}$ and $\mathrm{ZnSO_4}$.[16] This gives $\Delta H^{\ominus}_{\mathrm{sol}}(\mathrm{CoSO_4{\cdot}7H_2O,\ s}) = 11.1$ kJ mol^{-1}. The solubility[87] and entropy[89] of the heptahydrate together with osmotic and activity coefficients[69,70] obtained by combining data on both $\mathrm{CoSO_4}$ and $\mathrm{NiSO_4}$ give $\Delta G^{\ominus}_{\mathrm{sol}}(\mathrm{CoSO_4.7H_2O,\ s}) = 13.3$ kJ mol^{-1}, $\Delta S^{\ominus}_{\mathrm{sol}}(\mathrm{CoSO_4.7H_2O,\ s}) = -7.4$ J K^{-1} mol^{-1}, and $S^{\ominus}(\mathrm{Co^{2+},\ aq}) = -110$ J K^{-1} mol^{-1}. The average of our two values is $S^{\ominus}(\mathrm{Co^{2+},\ aq}) = -111 \pm 5$ J K^{-1} mol^{-1} which, with our selected $\Delta H_f^{\ominus}(\mathrm{Co^{2+},aq})$, gives $\Delta G_f^{\ominus}(\mathrm{Co^{2+},aq}) = -55.7 \pm 1.5$ kJ mol^{-1} and $E^{\ominus}(\mathrm{Co^{2+}|Co}) = -0.289 \pm 0.008$ V.

Cobalt(III)

Previous calculations[90] were adjusted to fit the data on $\mathrm{Co^{2+}(aq)}$, $\mathrm{Fe^{2+}(aq)}$, and $\mathrm{Fe^{3+}(aq)}$ given elsewhere in this work. This yields $\Delta G_f^{\ominus}(\mathrm{Co^{3+},aq}) = 130.4 \pm 4$ kJ mol^{-1}, $\Delta H_f^{\ominus}(\mathrm{Co^{3+},aq}) = 76 \pm 7$ kJ mol^{-1}, and $S^{\ominus}(\mathrm{Co^{3+},\ aq}) = -348 \pm 25$ J K^{-1} mol^{-1}.

Nickel(II)

If the data of Haring and Vandenbosche[91] are updated and combined with more recent activity coefficients,[69] we find $E^{\ominus}(\mathrm{Ni^{2+}|Ni}) = -0.239$ V and $\Delta G_f^{\ominus}(\mathrm{Ni^{2+},aq}) = -46.2$ kJ mol^{-1}. $\Delta H_f^{\ominus}(\mathrm{Ni^{2+},aq})$ can be obtained from the value[58,92] $\Delta H_f^{\ominus}(\mathrm{NiCl_2,\ s}) = -304.86 \pm 0.2$ kJ mol^{-1} and a heat of solution. For the solution process, Leonidov and Furkaluk[86] give $\Delta H^{\ominus}_{\mathrm{sol}}(\mathrm{NiCl_2,\ s}) = -85.0$ kJ mol^{-1}. The origin of the NBS value for this quantity has been described by Archer.[93] We have followed the same route but added more recent work[77] to the heat of dilution data. A Pitzer parameter fit gave $^{\Phi}L = 0.52$ kJ mol^{-1} at a dilution of $\mathrm{NiCl_2{\cdot}20000H_2O}$, which yields $\Delta H^{\ominus}_{\mathrm{sol}}(\mathrm{NiCl_2,\ s}) = -83.07$ kJ mol^{-1}. With the average value, $\Delta H^{\ominus}_{\mathrm{sol}}(\mathrm{NiCl_2,\ s}) = -84.0 \pm 1.2$ kJ mol^{-1}, we find $\Delta H_f^{\ominus}(\mathrm{Ni^{2+},aq}) = -54.7 \pm 1.2$ kJ mol^{-1} and $S^{\ominus}(\mathrm{Ni^{2+},\ aq}) = -129$ J K^{-1} mol^{-1}.

Two other values of this entropy can be obtained by using solution data on $\mathrm{NiSO_4{\cdot}7H_2O}$ and α-$\mathrm{NiSO_4{\cdot}6H_2O}$. The standard enthalpies of solution[88,94] are 12.49 and 4.81 kJ mol^{-1}, respectively. The solubilities[68] and the osmotic and activity coefficients[69,70] at 298.15 K yield $\Delta G^{\ominus}_{\mathrm{sol}}(\mathrm{NiSO_4{\cdot}7H_2O,\ s}) = 12.91$ kJ mol^{-1} and $\Delta G^{\ominus}_{\mathrm{sol}}(\alpha\text{-}\mathrm{NiSO_4{\cdot}6H_2O,\ s}) = 12.64$ kJ mol^{-1}. Then from the entropies of the two solids[94] we find, from $\mathrm{NiSO_4{\cdot}7H_2O(s)}$, that $S^{\ominus}(\mathrm{Ni^{2+},\ aq}) = -131$ J K^{-1} mol^{-1} and, from α-$\mathrm{NiSO_4{\cdot}6H_2O}$, $S^{\ominus}(\mathrm{Ni^{2+},\ aq}) = -130$ J K^{-1} mol^{-1}. Our selected value is $S^{\ominus}(\mathrm{Ni^{2+},\ aq}) = -130.0 \pm 2$ J K^{-1} mol^{-1}.

Gallium(III)

From the work of Saltman and Nachtrieb,[95] $E^{\ominus}(\mathrm{Ga^{3+}|Ga}) = -0.560 \pm 0.01$ V, whence $\Delta G_f^{\ominus}(\mathrm{Ga^{3+},aq}) = -162 \pm 3$ kJ mol^{-1}. The temperature coefficient of the potential was -0.566 mV K^{-1}, which gives $S^{\ominus}(\mathrm{Ga^{3+},\ aq}) = -319$ J K^{-1} mol^{-1}.

A second value can be obtained from data on gallium trichloride. Klemm and Jacobi[96] found $\Delta H_f^{\ominus}(\mathrm{GaCl_3,\ s}) = -523 \pm 4$ kJ mol^{-1}. Recent studies of the thermodynamics of gallium(III) in chloride media have encountered difficulties[97] that, as stability constants[98] suggest, can be partly attributed to both hydrolysis and, at moderate chloride concentrations, chloride complexing. van Gaans and van Miltenburg[99] studied the heats of solution and dilution of gallium trichloride over a wide range of acid and chloride concentrations. They made corrections for hydrolysis; chloride complexing was allowed for by using Pitzer parameters for an extrapolation to infinite dilution. They found $\Delta H^{\ominus}_{\mathrm{sol}}(\mathrm{GaCl_3,\ s}) = -197.5$ kJ mol^{-1}. This gives $\Delta H_f^{\ominus}(\mathrm{Ga^{3+},aq}) = -219$ kJ mol^{-1} and hence $S^{\ominus}(\mathrm{Ga^{3+},\ aq}) = -347$ J K^{-1} mol^{-1}.

A third value can be calculated from studies of the equilibrium constant of the reaction:

$$\mathrm{GaOOH(s) + 3H^+(aq) = Ga^{3+}(aq) + 2H_2O(l)} \qquad (12)$$

Bénézeth et al.[100] determined values at 150 and 60 °C and at infinite dilution ($K^{\ominus}$). They thereby calculated $S^{\ominus}(\mathrm{Ga^{3+},\ aq}) = -205$ J K^{-1} mol^{-1}. This is clearly far too positive. However, additional values of $K^{\ominus}$ at other temperatures exist.[101−103] We have also obtained values by correcting those equilibrium quotients of Craig and Tyree[104] that were obtained at ionic strengths less than 0.25 M, both for hydrolysis and to infinite dilution. We used Bénézeth et al.'s first hydrolysis constants and their extended Debye−Huckel method of interconverting a stability constant between zero and low ionic strengths.[100] The same selective procedure was applied to the data of Uchida and Okuwaki,[105] who neglected chloride complexing. Only the two samples of lowest chloride concentration (<0.1 m) were considered. The resulting set of equilibrium constants is shown in Table 6. From these data, we find $\Delta G^{\ominus}(12) = -16.7$ kJ mol^{-1}, $\Delta H^{\ominus}(12) = -75.3$ kJ mol^{-1}, and $\Delta S^{\ominus}(12) = -197$ J K^{-1} mol^{-1}. The entropy of the solid[106] then yields $S^{\ominus}(\mathrm{Ga^{3+},\ aq}) = -286$ J K^{-1} mol^{-1}. We take the average of our three values, which gives $S^{\ominus}(\mathrm{Ga^{3+},\ aq}) = -317 \pm 25$ J K^{-1} mol^{-1}.

Table 6. Values of the Solubility Product of GaOOH(s) at Various Temperatures

temperature/°C	$\log_{10} K^{\ominus}$	ref
25	2.9	101, 102
50	2.3	104
60	0.87	100, 106
60	1.7	103
75	1.5	104
100	−0.38	105
150	−0.70	100, 106

Indium(III)

The NBS data[16] for $\mathrm{In^{3+}(aq)}$ are not internally consistent, and their quoted value, $S^{\ominus}(\mathrm{In^{3+},\ aq}) = -151$ J K^{-1} mol^{-1}, seems far too positive. Helgeson and Kirkham[107] cite Wagman, who communicated a corrected value (−264 J K^{-1} mol^{-1}). The following pathway gives a figure in close agreement.

Recent data[108] give $E^{\ominus}(\mathrm{In^{3+}|In}) = -0.3371 \pm 0.003$ V, whence $\Delta G_f^{\ominus}(\mathrm{In^{3+},aq}) = -97.6 \pm 1$ kJ mol^{-1}. Klemm and Brautigam[109] found $\Delta H_f^{\ominus}(\mathrm{InCl_3,\ s}) = -537.6 \pm 4$ kJ mol^{-1}. Calculation of $\Delta H_f^{\ominus}(\mathrm{In^{3+},\ aq})$ from heats of solution of $\mathrm{InCl_3}$[110−112] is made difficult by the formation of an indium−chloride complex, $\mathrm{InCl^{2+}(aq)}$, for which enthalpy data have not been determined. A quite recent review[98] recommends a formation constant $K^{\ominus}$ of 560 for the complex and suggests that at the dilutions of interest, $\mathrm{In^{3+}(aq)}$, $\mathrm{InCl^{2+}(aq)}$, and $\mathrm{In(OH)Cl^{+}(aq)}$ are the solution components, the second of these three being predominant. We have combined this information with pH values of $InCl_3$(aq) given by Moeller[113] to calculate the compositions of the relevant solutions. At each stage in the iterative calculation, the equilibrium quotient for the formation of $InCl^{2+}$ was compared with the value obtained from $K^\ominus$ by using extended Debye−Huckel theory in the form recommended by Bénézeth et al.[100] After five cycles, the difference was negligible.

A value of $\Delta H^\ominus$ for the formation of $InCl^{2+}$(aq) from In^{3+}(aq) was obtained by assuming that $\Delta S^\ominus = 56$ J K^{-1} mol^{-1}, a figure obtained from the analogous thallium reaction.[16,114] We then combined the result with the observed difference in the heats of solution of $InCl_3$ in water and in 0.1 M HCl to comparable dilutions[112] to obtain an approximate value of $\Delta H^\ominus$ for the formation of $In(OH)Cl^+$(aq) from In^{3+}(aq). We were then able to correct each heat of solution to the composition $[In^{3+}(aq) + 3Cl^-(aq)]$ and use data on $LaCl_3$(aq) to make the small adjustments to infinite dilution, Roth and Buchner's figures[110] being corrected to 25 °C with heat capacity data for gallium. Our three values for the standard enthalpy of solution of $InCl_3$(s) were −94 kJ mol^{-1} (ref 112), −97 kJ mol^{-1}(ref 111), and −103 kJ mol^{-1}(ref 110). Because the dilutions were less precisely specified in the data given in ref 112, we have weighted these three values in the ratio 1:2:2 and take $\Delta H^\ominus_{sol}(InCl_3, s) = -99 \pm 5$ kJ mol^{-1}. Thus, $\Delta H_f^\ominus(In^{3+}, aq) = -135 \pm 7$ kJ mol^{-1} and $S^\ominus(In^{3+}, aq) = -264 \pm 25$ J K^{-1} mol^{-1}.

Thallium(III)

For the thallium(I) redox potential,[115] we take $E^\ominus(Tl^+|Tl) = -0.327 \pm 0.002$ V, which gives us $\Delta G_f^\ominus(Tl^+, aq) = -31.56 \pm 0.2$ kJ mol^{-1}. Stonehill[116] reviewed and added to previous work on $E^\ominus(Tl^{3+}|Tl^+)$ and recommended 1.280 ± 0.01 V, which was adopted by the NBS.[16] Consequently, $\Delta G_f^\ominus(Tl^{3+},aq) = 215.4 \pm 2$ kJ mol^{-1}.

The NBS value for $\Delta H_f^\ominus(Tl^{3+}, aq)$ seems to be based upon the work of Thomsen,[117] who studied the reduction of a solution with the composition $TlBr_3{\cdot}0.703HBr{\cdot}420H_2O$ by excess $SO_2{\cdot}200H_2O$ at 19.1 °C, the products being TlBr(s), $HBr{\cdot}320H_2O$, and $H_2SO_4{\cdot}860H_2O$. The situation is complicated by the fact that Tl^{3+}(aq) forms very stable complexes with bromide. The relevant stability constants[118] suggest that the composition of the initial thallium(III) solution is 0.05% $[TlBr_2]^+$, 28.9% $[TlBr_3]$, and 70.6% $[TlBr_4]^-$.

We now try to correct Thomsen's results to 25 °C. The dominant reaction is

$$\begin{aligned} & TlBr_4^-(aq) + SO_2(aq) + 2H_2O(l) \\ & \quad = TlBr(s) + H_2SO_4(aq) + 2HBr(aq) + Br^-(aq) \end{aligned}$$

Because H_2SO_4(aq) and HBr(aq) are ionized, we expect the reaction to have a large negative value of ΔC_p. From experimental[119−121] and estimated[122] values of heat capacities, we estimate $\Delta C_p = -600 \pm 200$ J K^{-1} mol^{-1}. Combining this figure with a correction for the heat of dilution of the excess SO_2, Thomsen's value for the reduction of $TlBr_3{\cdot}0.703HBr{\cdot}420H_2O$ becomes $\Delta H = -154.4$ kJ mol^{-1} at 25 °C. It can be combined with our calculated composition of the thallium(III) solution, the necessary auxiliary data, including a new value of $\Delta H_f^\ominus(TlBr, s)$,[123] and the enthalpies of complexing[114] to provide an enthalpy of formation of $\{Tl^{3+}(aq) + 3Br^-(aq)\}$ at the cited concentration. We have estimated a correction to infinite dilution of −5.5 kJ mol^{-1} from data on heats of solution of lanthanide trichlorides and tribromides.[16,124] This gives $\Delta H_f^\ominus\{Tl^{3+}(aq) + 3Br^-(aq)\} = -174 \pm 8$ kJ mol^{-1} and $\Delta H_f^\ominus(Tl^{3+}, aq) = 190 \pm 8$ kJ mol^{-1}. Hence, $S^\ominus(Tl^{3+}, aq) = -217 \pm 25$ J K^{-1} mol^{-1}.

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Notes

The authors declare no competing financial interest.

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Equation 8 was incorrect in the version published ASAP May 23, 2012. The correct version reposted May 24, 2012.