Thermodynamic Properties of Co^{3+}(aq)

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Improved values of the thermodynamic properties of Co^{3+}(aq) at 298.15 K have been calculated: $\Delta_f H^{\ominus}_m(Co^{3+},aq) = 79 \pm 7$ kJ mol^{-1};$\Delta_f G^{\ominus}_m(Co^{3+},aq) = 131 \pm 4$ kJ mol^{-1}; $S^{\ominus}_m(Co^{3+},aq) = -341 \pm 25$ J K^{-1} mol^{-1}. The value of $S^{\ominus}_m(Co^{3+},aq)$ is considerably more negative than that of $S^{\ominus}_m(Fe^{3+},aq)$, a difference which can be related mainly to the small ionic radius associated with the d^6 low-spin state. Other calculations suggest that the stabilizations with respect to the high-spin state are $\Delta H^{\ominus}_m = 46 \pm 20$ kJ mol^{-1} and $\Delta G^{\ominus}_m = 38 \pm 25$ kJ mol^{-1}.

The thermodynamic properties of the blue aqueous ion Co^{3+}(aq) are of particular interest. One reason is that it is the only dipositive or tripositive aqueous ion of the first transition series which occurs in the low-spin state.[1,2] Another is that its stabilization with respect to the high-spin state has a crucial bearing on competing explanations of the anomalous rates of its electron-transfer reactions.[3,4] Unfortunately Co^{3+}(aq) slowly oxidizes water, and this has made its thermodynamic properties both hard to determine and a matter of dispute. In this paper, we show how recent work can be used to calculate more reliable values of $\Delta_f H^{\ominus}_m(Co^{3+},aq)$, $\Delta_f G^{\ominus}_m(Co^{3+},aq)$, $S^{\ominus}_m(Co^{3+},aq)$, and $E^{\ominus}(Co^{3+}–Co^{2+})$ than were previously obtainable. We also argue that these data are consistent with theoretical expectations arising from the magnetic and spectroscopic properties of the complex $[Co(H_2O)_6]^{3+}$, and discuss the stabilization of the complex with respect to the high-spin state.

Auxiliary Data

Unless otherwise stated, thermodynamic data were taken from ref. 5. For data on Co^{2+}(aq), Fe^{2+}(aq), and Fe^{3+}(aq), see Table 1.

The Value of $\Delta_f H^{\ominus}_m(Co^{3+},aq)$.—Three values[6–8] exist for ΔH_m of reaction (1), but the best is that of Mowforth *et al.*[8] who worked at 25 °C in 2.7 mol dm^{-3} $HClO_4$, and improved the methods of correcting for dilution effects.

$$Co^{3+}(aq) + Fe^{2+}(aq) \longrightarrow Co^{2+}(aq) + Fe^{3+}(aq) \quad (1)$$

Other data[9] suggest that at these acidities, the correction for hydrolysis is very small, and because of similarities in the constitution of the reactants and products we assume a zero correction to infinite dilution. This gives $\Delta H^{\ominus}_m(1) = -94 \pm 6$ kJ mol^{-1} and thus $\Delta_f H^{\ominus}_m(Co^{3+},aq) = 79 \pm 7$ kJ mol^{-1}. An almost identical value (77 kJ mol^{-1}) is obtained from the temperature variation of the formal potential[10] of the electrode Co^{3+}–Co^{2+} in 3 mol dm^{-3} $HClO_4$, but as the data were minimal we have not weighted this in our assessment.

Table 1. Thermodynamic properties of the aqueous dipositive and tripositive ions of iron and cobalt

	$\Delta_f H^{\ominus}_m$ / kJ mol^{-1}	$\Delta_f G^{\ominus}_m$ / kJ mol^{-1}	$S^{\ominus}_m$ / J K^{-1} mol^{-1}
Fe^{2+}(aq)	-91.2 ± 1.5^a	-89.8 ± 1.5^b	-108 ± 4^c
Fe^{3+}(aq)	-48.5 ± 3^d	-15.4 ± 1.5^e	-280 ± 10^b
Co^{2+}(aq)^f	-58.2 ± 2	-55.6 ± 2	-109 ± 9
Co^{3+}(aq)^g	79 ± 7	131 ± 4	-341 ± 25

[a] A value was obtained by combining the heat of formation of $FeCl_2$ given by M. F. Koehler and J. P. Coughlin, *J. Phys. Chem.*, 1959, **63**, 605, with the average of the heats of solution of J. C. M. Li and N. W. Gregory, *J. Am. Chem. Soc.*, 1952, **74**, 4670, and of P. J. Cerutti and L. G. Hepler, *Thermochim. Acta*, 1977, **20**, 309, corrected in the former case to infinite dilution using data on $NiCl_2$. This was doubly weighted against the values of J. W. Larson, P. Cerutti, H. K. Garber, and L. G. Hepler, *J. Phys. Chem.*, 1968, **72**, 2902 and V. P. Vasil'ev, N. G. Dmitrieva, P. N. Vorob'ev, V. N. Vasil'eva, and I. I. Nechaeva, *Zh. Neorg. Khim*, 1985, **30**, 1681. [b] Calculated from the other two entries in this row. [c] The average of the value of J. W. Larson *et al.*, ref. *a*, and that obtained by combining our first value of $\Delta_f H^{\ominus}_m(Fe^{2+},aq)$, with the $E^{\ominus}(Fe^{2+}–Fe)$ of P. R. Tremaine and J. C. Le Blanc, *J. Solution Chem.*, 1980, **9**, 415. [d] From the $\Delta H^{\ominus}_m$ value for Fe^{3+}–Fe^{2+} of D. O. Whittemore and D. Langmuir, *J. Chem. Eng. Data*, 1972, **17**, 288. [e] From $E^{\ominus}(Fe^{3+}–Fe^{2+}) = 0.771$ V, the average of the values reviewed in ref. *d*. [f] R. N. Goldberg, R. G. Riddell, M. R. Wingard, H. P. Hopkins, C. A. Wulff, and L. G. Hepler, *J. Phys. Chem.*, 1966, **70**, 706. [g] See text.

The Values of $\Delta_f G^{\ominus}_m(Co^{3+},aq)$ *and* $E^{\ominus}(Co^{3+}–Co^{2+})$.—The value of $E^{\ominus}(Co^{3+}–Co^{2+})$ has been a matter of dispute for some time, and figures as different as 1.30 and 1.95 V have been proposed. We first ignore those data[7,11] which are inconsistent with the oxidizing strength[6] of Co^{3+}(aq). We then confine ourselves to measurements made in perchlorate media where complexing by the anion is small. Zingales and coworkers[12] determined the formal potential $E_f(Co^{3+}–Co^{2+}) = 1.841 \pm 0.002$ V in 5.1 mol dm^{-3} $HClO_4$ at 268.15 K using a cell without a liquid junction. [equation (2)]. Using our

$$Co^{3+}(aq) + \tfrac{1}{2}H_2(g) \longrightarrow Co^{2+}(aq) + H^+(aq) \quad (2)$$

recommended value $\Delta H^{\ominus}_m(2) = -137$ kJ mol^{-1} in the Gibbs–Helmholtz equation then yields $E_f(Co^{3+}–Co^{2+}) = 1.888$ V at 298.15 K in 5.1 mol dm^{-3} $HClO_4$. To convert this into a value at infinite dilution, we combine our value $E^{\ominus}(Fe^{3+}–Fe^{2+}) = 0.771$ V with the corresponding formal potential, obtained by correcting Fe^{3+}–Fe^{2+} potentials in various concentrations of perchloric acid[13–16] for the hydrolysis of Fe^{3+}(aq)[17] and extrapolating them to 5.1 mol dm^{-3} $HClO_4$. The correction is 0.035 V and it gives $E^{\ominus}(Co^{3+}–Co^{2+}) = 1.923$ V. A similar correction can be made to the formal potentials obtained by Warnqvist[10,18] in 3 and 4 mol dm^{-3} $HClO_4$ using cells with a liquid junction. The resulting values are 1.90 and 1.96 V respectively. Weighting the three figures as 2:1:1, we obtain

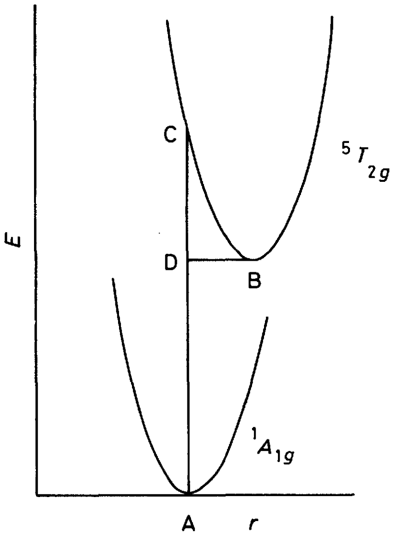

Figure. Potential-energy curves for the $^1A_{1g}$ and $^5T_{2g}$ states of $[Co(H_2O)_6]^{3+}$

$E^\circ(Co^{3+}-Co^{2+}) = 1.93 \pm 0.03$ V and $\Delta_f G^\circ_m(Co^{3+},aq) = 131 \pm 4$ kJ mol^{-1}.

The Value of $S^\circ_m(Co^{3+},aq)$.—This can be calculated from our $\Delta_f H^\circ_m(Co^{3+},aq)$ and $\Delta_f G^\circ_m(Co^{3+},aq)$: the result is $S^\circ_m(Co^{3+},aq) = -341 \pm 25$ J K^{-1} mol^{-1}.

Discussion

The thermodynamic properties of Co^{3+}(aq) appear in Table 1; their most striking feature is the low, negative value of $S^\circ_m(Co^{3+},aq)$. This quantity is about 60 J K^{-1} mol^{-1} smaller than $S^\circ_m(Fe^{3+},aq)$ even though the entropies of the dipositive aqueous ions are very similar. Such a difference is precisely what is predicted by empirical equations which relate the entropies of aqueous ions to charge, relative atomic mass, and crystal radius.[19,20] When in its d^6 low-spin state, Co^{3+} forms unusually short bonds. This is explained by ligand field theory,[2] and is apparent, for example, in metal–oxygen distances in the complexes $[M(H_2O)_6]^{3+}$ which are found in alums with the formula type $CsM(SO_4)_2 \cdot 12H_2O$.[21] Likewise, the ionic radius of low-spin Co^{3+} in octahedral co-ordination is smaller than that of any other tripositive ion of the first transition series. Shannon[22] recommends radii of 64.5 and 54.5 pm for high-spin Fe^{3+} and low-spin Co^{3+} respectively. The best-known empirical equation for the entropies of aqueous ions is that of Powell and Latimer.[19] It should include a magnetic entropy term, $S_{m,mag}$. For aqueous transition-metal ions, $S_{m,mag}$ is often uncertain, but both high-spin Fe^{3+} and low-spin Co^{3+} have ground states which are not split by a ligand field, so the $S_{m,mag}$ values can be specified precisely as $R\ln 6$ and $R\ln 1$ respectively. With Shannon's ionic radii, the Powell–Latimer equation then gives $S^\circ_m(Fe^{3+},aq) - S^\circ_m(Co^{3+},aq) = 53$ J K^{-1} mol^{-1} in good agreement with our experimental value. A more recent equation proposed by Morss[20] yields a very similar figure (52 J K^{-1} mol^{-1}).

The Stabilization of Low-spin $[Co(H_2O)_6]^{3+}$(aq) *with respect to the High-spin State.*—The ion $[Co(H_2O)_6]^{3+}$ exchanges water molecules with the solvent, and electrons with $[Co(H_2O)_6]^{2+}$, at unexpectedly high rates. As $[Co(H_2O)_6]^{2+}$(aq) is very labile, and is always present in solutions of $[Co(H_2O)_6]^{3+}$, an explanation of the fast electron-transfer reaction could account for both anomalies. The origin of such an explanation might lie in a spin equilibrium, if the labile, high-spin $^5T_{2g}$ state lies <20 kJ mol^{-1} above the $^1A_{1g}$ ground state.[1,3,4] However, Johnson and Sharpe[2] assigned bands in the spectrum of $CsCo(SO_4)_2 \cdot 12H_2O$ and calculated a value of 60 kJ mol^{-1} for the $^1A_{1g} \longrightarrow {}^5T_{2g}$ transition energy. They noted that the transition occurs at fixed internuclear distance, a fact which by itself suggests that its energy provides an upper limit for the thermodynamic stablization, but they preferred to adopt 60—85 kJ mol^{-1} as a best estimate of the stabilization because of other approximations involved in the calculation of the transition energy.

More recently, Winkler *et al.*[23] took Johnson and Sharpe's transition to be the energy AC in the Figure, and tried to correct it by calculating the energy CD. They obtained $E_{CD} = 43$ kJ mol^{-1}, and thus $E_{AD} = 17$ kJ mol^{-1} for the thermodynamic stabilization energy, a value low enough to be consistent with spin-equilibrium involvement in the anomalous reaction kinetics. The calculation required the symmetric Co–O stretching frequency in the $^5T_{2g}$ state, and a figure of 357 cm^{-1} was estimated by reducing the value observed in the ground state of a Tutton salt of cobalt(II) by 10%. It is now known that compounds containing the tripositive ions $[M(H_2O)_6]^{3+}$ show symmetric stretching frequencies in the range 510—540 cm^{-1}.[24] If Winkler, *et al.*'s calculation is repeated with such values, then E_{CD} exceeds 60 kJ mol^{-1}, and contradicts the experimental evidence[1,2] by making $^5T_{2g}$ the ground state. Clearly their method substantially overestimates the correction.

An alternative approach relies on the valence force-field approximation,[25] and writes the potential energy for the totally symmetric vibration of the $^5T_{2g}$ state in the form (3), where Δr

$$V = 6[\tfrac{1}{2}k(\Delta r)^2] \quad (3)$$

is the displacement from the equilibrium internuclear distance during the vibration and k is the force constant. Then, we can write equation (4) where ν is the stretching frequency, $m(H_2O)$

$$E_{CD} = 3k(\Delta r_e)^2 = 12\pi^2\nu^2 m(H_2O)(\Delta r_e)^2 \quad (4)$$

is the mass of a water molecule, and Δr_e is the difference between the equilibrium internuclear distances in the $^1A_{1g}$ and $^5T_{2g}$ states.

There are several possible ways of estimating Δr_e. Shannon's value for the difference in the ionic radii of high-spin and low-spin Co^{3+} is 6.5 pm.[22] An estimate for $[Co(H_2O)_6]^{3+}$ made by using data from the alums is 7.0 pm.[21] We have estimated the cobalt–oxygen distance in the high-spin complex from a linear plot of the ionic radii of the high-spin ions in octahedral co-ordination[22] against the metal–oxygen distances[21] in the caesium alums of Ti, V, Cr, Mn, Fe, and Ga. This yields 194.3 pm and $\Delta r_e = 7.0$ pm. If, instead of ionic radii, one uses the metal–fluorine distances in the high-spin trifluorides,[26–28] the Δr_e value becomes 7.7 pm. We take $\Delta r_e = 7.0 \pm 1.5$ pm. To obtain ν, we substitute our estimated cobalt–oxygen distance in high-spin $CsCo(SO_4)_2 \cdot 12H_2O$ into Figure 5 of ref. 24. This yields $\nu \approx 530$ cm^{-1}, and studies of $[Al(H_2O)_6]^{3+}$ suggest that the value will be lowered to about 510 cm^{-1} in aqueous solution.[24] Equation (4) then yields $E_{CD} = 24 \pm 10$ kJ mol^{-1}, and hence $E_{AD} = 36 \pm >10$ kJ mol^{-1} for the thermodynamic stabilization energy. This estimate relies on Johnson and Sharpe's calculation[2] of the energy of the two-electron transition from those of one-electron transitions using the strong-field approximation. Because of possible sources of error in the calculation, other than the one corrected for,* we have tried to

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* An obvious source of error is the neglect of vibrational changes, but these are largely expected to cancel one another out. More difficult to assess are the errors in ligand-field theory which is used to obtain AC.

Table 2. Thermodynamic properties of some tripositive aqueous ions

	$\Delta_f H^{\ominus}_m$ kJ mol^{-1}	$\Delta_f G^{\ominus}_m$ kJ mol^{-1}	$S^{\ominus}_m$ J K^{-1} mol^{-1}
Sc^{3+}(aq)	-647[a]		-255[b]
V^{3+}(aq)	-281[c]	-242[d]	-299[e]
Cr^{3+}(aq)[f]	-236		
Mn^{3+}(aq)	-104[c]	-74[g]	-267[e]
Fe^{3+}(aq)[h]	-48.5		-280
Ga^{3+}(aq)[i]	-218		

[a] The results of J. M. Stuve, *U.S. Bur. Mines. Rep. Invest.* 6705, 1965, and of E. J. Huber, G. C. Fitzgibbon, E. L. Head, and C. E. Holley, *J. Phys. Chem.*, 1963, **67**, 1731 give $\Delta_f H^{\ominus}_m(ScCl_3,s) = -942.2 \pm 2$ kJ mol^{-1}. This was combined with the heat of solution of J. Burgess and J. Kijowski, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2389, corrected to infinite dilution using data for $LaCl_3$. [b] Ref. 5. [c] Calculated from the two other figures in this row. [d] From the $E^{\ominus}(VO^{2+}–V^{3+})$ value of G. Jones and J. H. Colvin, *J. Am. Chem. Soc.*, 1944, **66**, 1563, and $\Delta_f G^{\ominus}_m(VO^{2+},aq)$ of ref. 5. [e] Estimated; see text. [f] Only reactions of well established stoicheiometry were considered. The enthalpy of oxidation of Fe^{2+}(aq) by H^+(aq) in 0.5 mol dm^{-3} $HClO_4$ is 40.8 ± 1.5 kJ mol^{-1} according to R. Connick and W. H. McVey, *J. Am. Chem. Soc.*, 1951, **73**, 1798, and the work of B. J. Fonatana cited therein. This was used to calculate two values for the enthalpy of reduction of $HCrO_4^-$(aq) by hydrogen in 0.5 mol dm^{-3} $HClO_4$ from the results of M. W. Evans, 'The Transuranium Elements,' eds. G. T. Seaborg, J. T. Katz, and W. M. Manning, McGraw-Hill, New York, 1949, part I, pp. 282—294, and of I. Dellien and L. G. Hepler, *Can. J. Chem.*, 1976, **54**, 1383 with a correction in the former case for the presence of H_2CrO_4(aq) based upon the data of I. Dellien, F. M. Hall, and L. G. Hepler, *Chem. Rev.*, 1976, **76**, 283. The average gives the datum in Table 2 when the extrapolation to infinite dilution is neglected. A value 15 kJ mol^{-1} more negative has been obtained by I. Dellien *et al.* from heats of oxidation of Cr^{2+} by Fe^{3+} and Cu^{2+} in 0.5 mol dm^{-3} $HClO_4$, but there is a considerable uncertainty in $\Delta_f H^{\ominus}_m(Cr^{2+}$, aq), and some oxidation of Cr^{2+} by ClO_4^- may have occurred (*cf.* G. Biedermann and V. Romano, *Acta Chem. Scand., Ser. A*, 1975, **29**, 615). [g] From $\Delta_f G^{\ominus}_m(Mn^{2+},aq)$ of ref. 5 and $E^{\ominus}(Mn^{3+}–Mn^{2+}) = 1.60$ V given by G. Biedermann and R. Palombari, *Acta Chem. Scand., Ser. A*, 1978, **32**, 381. [h] See Table 1. [i] The heat of solution of $GaCl_3$ given by W. A. Roch and A. Buchner, *Z. Electrochem.*, 1934, **40**, 87, was corrected to 25 °C and infinite dilution using $\Delta C^{\ominus}_p$ data for $GdCl_3$, and heat of dilution data for $LaCl_3$. It was then combined with $\Delta_f H^{\ominus}_m(GaCl_3,s)$ from W. Klemm and H. Jacobi, *Z. Anorg. Allg. Chem.*, 1932, **207**, 177.

Table 3. Values of $\Delta H^{\ominus}_m$(kJ mol^{-1}) for reactions (5)—(7)[a] at 298.15 K

M	$\Delta H^{\ominus}_m(5)$[b]	$\Delta H^{\ominus}_m(6)$[c]	$\Delta H^{\ominus}_m(7)$[d]
Sc	$-5\,299$	$-8\,001$	$-5\,516$
V	$-5\,706$	$-8\,463$	
Cr	$-5\,884$	$-8\,638$	$-6\,042$
Mn	$-5\,880$	$-8\,638$	$-6\,047$
Fe	$-5\,761$	$-8\,532$	$-5\,939$
Co		$-8\,729$	$-6\,108$
Ga	$-6\,035$	$-8\,830$	$-6\,214$

[a] All values were obtained using $\Delta_f H^{\ominus}_m(M^{3+},g)$ of ref. 5. [b] $\Delta_f H^{\ominus}_m(M^{3+},aq) - \Delta_f H^{\ominus}_m(M^{3+},g)$. [c] From equation (1) of ref. 31, using the data recommended there, except for $\Delta_f H^{\ominus}_m(M^{3+},g)$. [d] From the values of $\Delta_f H^{\ominus}_m(MF_3,s)$ and $\Delta_f H^{\ominus}_m(F^-,g)$ recommended in ref. 31.

Table 4. Thermodynamic properties of high-spin and low-spin Co^{3+} (aq)

	$\Delta_f H^{\ominus}_m$ kJ mol^{-1}	$\Delta_f G^{\ominus}_m$ kJ mol^{-1}	$S^{\ominus}_m$ J K^{-1} mol^{-1}
Co^{3+}(aq, low spin)	79	131	-341
Co^{3+}(aq, high spin)	125	169	-314

$$M^{3+}(g) + \tfrac{3}{2}H_2(g) \longrightarrow M^{3+}(aq) + 3H^+(aq) + 3e^-(g) \quad (5)$$

$$M^{3+}(g) + 3K^+(g) + 6F^-(g) \longrightarrow K_3MF_6(s) \quad (6)$$

$$M^{3+}(g) + 3F^-(g) \longrightarrow MF_3(s) \quad (7)$$

obtain an independent value for the stabilization energy using the empirical methods of Karapet'yants.[29,30] This calls for experimental figures for $\Delta_f H^{\ominus}_m(M^{3+},aq)$, and those which are required and available are shown in Table 2. The values for V^{3+}(aq) and Mn^{3+}(aq) rely on estimated entropies obtained by interpolation. Interpolation is quite difficult because it is hard to separate the magnetic entropy from the remainder which includes a detectable ligand-field contribution. As the magnetic entropy of d^5 ions is well established, we have assumed that the magnetic entropies of M^{2+}(aq) and M^{3+}(aq) increase approximately uniformly from zero at d^0 to $R\ln 6$ at d^5, and then drop back approximately uniformly to zero at d^{10}. When these magnetic entropies are subtracted, the plot of the entropies of d^n tripositive ions against those of d^{n+5} dipositive ions ($n = 0 \longrightarrow 5$) was assumed to be approximately linear. The values of $S^{\ominus}_m(V^{3+},aq)$ and $S^{\ominus}_m(Mn^{3+},aq)$ in Table 2 were established by using this plot and then adding the required magnetic entropy.

The values of $\Delta_f H^{\ominus}_m(M^{3+},aq)$ in Table 2 and other data allow calculations of $\Delta H^{\ominus}_m$ at 298.15 K for reactions (5)—(7). The results are shown in Table 3. When $\Delta H^{\ominus}_m(5)$ is plotted, first against $\Delta H^{\ominus}_m(6)$ and then against $\Delta H^{\ominus}_m(7)$, two straight lines are obtained. On the K_3MF_6 plot, there are six points, the correlation factor is 0.999, and deviations from linearity are < 10 kJ mol^{-1}. On the MF_3 plot, there are five points, the correlation factor is 0.999, and deviations from linearity are < 15 kJ mol^{-1}.

Now the hexafluorometalate(III) compounds and the trifluorides are all high spin or very nearly so,[31] so the experimental $\Delta H^{\ominus}_m(6)$ and $\Delta H^{\ominus}_m(7)$ for cobalt can be inserted into the plots to obtain two values of $\Delta H^{\ominus}_m(5)$ for high-spin Co^{3+}(aq). These yield 131 and 143 kJ mol^{-1} respectively for $\Delta_f H^{\ominus}_m(Co^{3+}$,aq,high spin), figures which when combined with the low-spin datum of Table 1 give thermodynamic stabilization energies for the low-spin state of 52 and 64 kJ mol^{-1}. Because the K_3MF_6 plot contains more points, and has better linearity, we doubly weight the first of these figures against the second, and then take the mean of the result (56 kJ mol^{-1}) and the spectroscopic value given earlier. This yields 46 ± 20 kJ mol^{-1} which is our preferred value for the enthalpy of stabilization.

Table 4 contains the resulting data for both the high-spin and the low-spin aqueous ion. The entropy of Co^{3+}(aq,high spin) was estimated by assuming that it differs from $S^{\ominus}_m(Fe^{2+},aq)$ by the amount that $S^{\ominus}_m(Fe^{3+},aq)$ differs from $S^{\ominus}_m(Mn^{2+},aq)$. As expected, for reaction (8), $\Delta S^{\ominus}_m$ is positive because of an increase in ionic radius and magnetic entropy. The estimate

$$Co^{3+}(aq,low\ spin) \longrightarrow Co^{3+}(aq,high\ spin) \quad (8)$$

for $\Delta G^{\ominus}_m(8)$ is 38 ± 25 kJ mol^{-1} which corresponds to an equilibrium constant of 2×10^{-7} at 298.15 K. It lies above the upper threshold which is usually specified by those who invoke a spin-state equilibrium to account for the high rates of the electron-transfer reactions of Co^{3+}(aq), and in that respect, it favours other[32] explanations.

Finally, our recommended values for $\Delta G^\circ_m(8)$ and $\Delta H^\circ_m(8)$ are in agreement with the n.m.r. measurements of Navon[33] who concluded that $\Delta G^\circ_m(8) > 23$ kJ mol^{-1}, a lower threshold which is converted by our $\Delta S^\circ_m(8)$ into $\Delta H^\circ_m(8) > 31$ kJ mol^{-1}. Clack and Smith[34] obtained $\Delta H^\circ_m(8) = 223$ kJ mol^{-1} by a quantum-mechanical calculation, but this was for an *isolated* $[Co(H_2O)_6]^{3+}$ ion, and used an approximate method (INDO).

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Received 7th April 1989; *Paper* 9/01446B