Characterization of Inner- and Outer-sphere Complexes by Thermodynamics and Absorption Spectra. Part 1. Sulphato-complexes of the First-row Transition Elements

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The sulphato-complexes of the transition-metal ions Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} have been shown to be predominantly outer sphere, and $[Fe(SO_4)]^+$ has been classified as inner sphere, for I = 0 and 5 mol dm^{-3} at 25 °C. At I = 0, a linear free-energy relation (l.f.e.r.) between log K_1 for the formation of the sulphato- and for the monohydroxo-complexes allows the classifications to be rationalised. The l.f.e.r. also allows the sulphate ligand to be tentatively identified as unidentate in the inner-sphere complexes from comparisons with n-dentate ligands (n = 1—3). The Fuoss equation adequately describes the K_1 values for those complexes of sulphate and other ligands that are predominantly outer sphere in character. The inner- and outer-sphere character of the species at I = 5 mol dm^{-3}, deduced from spectrophotometric measurement of the formation constants, is similar to the pattern at I = 0. Large decreases in the entropy of formation of both inner- and outer-sphere species are attributed mainly to the reduced influence of the sulphate ligand on the structure of the medium.

A SPECTROPHOTOMETRIC study of the complex species formed between sulphate ions and Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Fe^{III} at ionic strengths from 1 to 5 mol dm^{-3} and from 25 to 60 °C has been made for calculation of the concentrations of the various species present in certain solutions used in hydrometallurgical processing. It was apparent that identification of the species as inner or outer sphere would be a useful classification, and, for this purpose, thermodynamic changes and the characteristics of the absorption spectra of the species have been used as criteria.

Since the formation of an inner-sphere complex between hard acceptors and hard donors involves the displacement of at least one water molecule from the inner co-ordination sphere of the cation, it has been suggested that the enthalpy and entropy changes should be generally much higher than for the formation of outer-sphere complexes.[1] The position of the absorption bands of the complex species in the spectrum was used by Smithson and Williams [2] to indicate inner- or outer-sphere character. Thus, a weak band shown by an aqua-ion in the visible spectrum arises from d–d transitions and will be affected only by close approach of the

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[1] S. Ahrland, *Co-ordination Chem. Rev.*, 1972, **8**, 21.

[2] J. M. Smithson and R. J. P. Williams, *J. Chem. Soc.*, 1958, 457.

ligands in inner-sphere complexes. The shift of the band to higher or lower energies depends on the position of the ligand in the spectrochemical series. However, the greater separation between donor and acceptor in outer-sphere complexes gives rise to charge-transfer (c.t.) bands of higher energy in the u.v. that may also be influenced considerably by an inner-sphere configuration. Gray [3] pointed out that absorption coefficients assist in the identification of absorption bands arising from *d–d* transitions or charge transfer. Thus, values of less than 200 dm^3 mol^{-1} cm^{-1} are very likely to arise from *d–d* transitions, whereas values above 1 000 dm^3 mol^{-1} cm^{-1} are expected to result from c.t. complexes. Intermediate values in the range 200—1 000 dm^3 mol^{-1} cm^{-1} may indicate weak c.t. bands or *d–d* bands having large absorption coefficients. Mironov *et al.*[4] suggested that formation constants derived from visible spectra should be identified with inner-sphere complexes and those deduced from u.v. spectra should be identified with the sum of the inner- and outer-sphere constants.

RESULTS

As a preliminary step in the investigation of the sulphato-complex species, it was necessary to choose the conditions so that, initially, practically none of the sulphate-ion concentration would be in the hydrogensulphate form to avoid possible complications caused by the presence of more than one ligand. In order to define these conditions, it was necessary to know the formation constants of the $[HSO_4]^-$ ion for the medium and temperature in use. These data were not available in the literature, and were obtained from spectrophotometric measurements. The thermodynamic values for $I = 5$ mol dm^{-3}, calculated from plots of log K_1 against $1/T$, are compared in Table 1 with published values at lower ionic strength.

TABLE 1

Thermodynamic data (kJ mol^{-1}) for the reaction $H^+ + [SO_4]^{2-} \longrightarrow [HSO_4]^-$ at 25 °C

I / mol dm^{-3}	$\Delta G^\ominus$	$\Delta H^\ominus$	$T\Delta S^\ominus$	Ref.
0	−11.3	24.0	35.4	1
1	−6.1	23.5	29.5	1
2	−6.2	23.2	29.3	1
5	−8.8	14.0	22.8	This work

From the stability constants for $[HSO_4]^-$ at 25 and 60 °C, 3 and 6% respectively of the total sulphate concentration will be in the form $[HSO_4]^-$ at pH 3. Significant hydrolysis of the metal ions is unlikely to occur below pH 3.5. Hence solutions were maintained at pH 3.0—3.5.

The Iron(II)*- and Manganese*(II)*–Sulphate Systems.*—The absorbance was not changed sufficiently by the presence of sulphate ion to allow the formation constants to be determined.

The Cobalt(II)*–Sulphate System.*—This system has not been investigated extensively. A recent study by Mironov *et al.*[4] gave 1.7 ± 0.2 dm^3 mol^{-1} for the sum of the first formation constants for the inner- and outer-sphere complexes in 3 mol dm^{-3} lithium perchlorate at 25 °C using solubility and potentiometric methods. The contribution from the inner-sphere complex was thought to be very small. There are several values in the 100—250 dm^3 mol^{-1} region for $I = 0$, assessed from cation-exchange,[5] freezing-point,[6] and amalgam-electrode methods.[7] No observable change in the visible spectrum of cobalt(II) perchlorate was reported when up to 0.25 mol dm^{-3} sulphate was added.[2] However, a slight increase in the band at 512 nm of a 0.5 mol dm^{-3} solution of $Co[ClO_4]_2$ at 25 °C and $I = 5$ mol dm^{-3} was observed in the presence of 1.0 mol dm^{-3} $[SO_4]^{2-}$. Although the absorbance changes were too small for use of equation (1) at 25 °C, they became large enough at 50 °C. Accordingly, a series of solutions at $I = 5$ mol dm^{-3} containing up to 1.5 mol dm^{-3} $[SO_4]^{2-}$ was examined at 50 and 70 °C. Formation constants and absorption coefficients were derived from linear plots of $1/c_L$ against $c_M/(A - \varepsilon_0 c_M)$ according to equation (1)[8]

$$\frac{1}{c_L} = K_1(\varepsilon_1 - \varepsilon_0)\frac{c_M}{A - \varepsilon_0 c_M} - K_1 \qquad (1)$$

where c_M and c_L are the respective total concentrations of metal ion and ligand, ε_0 and ε_1 are the respective absorption coefficients of the metal aqua-ion and the complex, and A is the absorbance of a 1-cm pathlength of the solution. A condition of the equation is that c_L can replace the free-ligand concentration because $c_L \gg c_M$. Although in this instance, $c_L \simeq c_M$ at the lowest value of c_L used in the cobalt(II) system, the results for K_1 and ε_1 were almost the same as those derived from the equation of Rose and Drago [9] in which no assumptions about the concentrations are required.

The reason for low absorbance changes at 25 °C is evident from the dependence on temperature of the difference between the absorption coefficients of Co^{2+} and $Co[SO_4]$. The K_1 values obtained at the various wavelengths are reasonably consistent (Table 2).

TABLE 2

Effect of temperature on K_1 and ε_1 for $Co[SO_4]$, and on ε_0 for $Co[ClO_4]_2$

		50 °C			70 °C		
I / mol dm^{-3}	λ / nm	K_1 / dm^3 mol^{-1}	ε_1 / dm^3 mol^{-1} cm^{-1}	ε_0 / dm^3 mol^{-1} cm^{-1}	K_1 / dm^3 mol^{-1}	ε_1 / dm^3 mol^{-1} cm^{-1}	ε_0 / dm^3 mol^{-1} cm^{-1}
5	510				2.4	5.7	5.0
	520	2.4	5.4	4.8	2.5	5.7	4.9
	540	2.2	3.9	3.3	2.6	4.4	3.5
	550	2.4	2.9	2.4	2.7	3.4	2.6
	560	2.5	2.0	1.6	2.7	2.5	1.8
Mean		2.4 ± 0.1			2.6 ± 0.1		

The Nickel(II)*–Sulphate System.*—Literature values for K_1 show the same pattern as that for the cobalt(II) system. Typical values for a medium of $I = 0$ are 219,[10] 209,[11] and 112 dm^3 mol^{-1} (ref. 7) using freezing-point and cell methods. A value of 3.7 dm^3 mol^{-1} was obtained by polarography for a medium of 1 mol dm^{-3} sodium perchlorate.[12] The constant for the outer-sphere complex at

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[3] H. B. Gray, *J. Chem. Educ.*, 1964, **41**, 2.

[4] V. E. Mironov, Yu. A. Makashev, I. Ya. Mavrina, and M. M. Kryzhanovskii, *Russ. J. Inorg. Chem.*, 1970, **15**, 668.

[5] R. G. Seys and C. B. Monk, *J. Chem. Soc.*, 1965, 2452.

[6] P. G. M. Brown and J. E. Prue, *Proc. Roy. Soc.*, 1955, **A232**, 320.

[7] B. J. Prasad, *J. Indian Chem. Soc.*, 1968, **45**, 1037.

[8] J. Paatero and L. Hummelstedt, *Acta Acad. Aboensis, Ser. B*, 1971, **31**, 1.

[9] N. J. Rose and R. S. Drago, *J. Amer. Chem. Soc.*, 1959, **51**, 6138.

[10] J. Kenttamaa, *Suomen Kem.*, 1956, **29B**, 59.

[11] V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 1959, 3934.

[12] N. Tanaka, Y. Saito, and H. Ogino, *Bull. Chem. Soc. Japan*, 1963, **36**, 794.

I = 3.0 mol dm^{-3}, measured using a $Hg_2[SO_4]$ electrode by Mironov *et al.*,[4] was 1.8 ± 0.2 dm^3 mol^{-1} with a value of *ca.* 0 for the inner-sphere complex.

There was no effect on the visible spectrum (bands at 390 and 720 nm) of 0.1 mol dm^{-3} $Ni[ClO_4]_2$ when 1.0 mol dm^{-3} $Na_2[SO_4]$ was added at I = 5 mol dm^{-3}. However, increase of the concentration of sodium sulphate from 0.1 to 1.0 mol dm^{-3} caused an increase in absorbance in the 205—220 nm region (Figure 1). A series of solutions containing up to 0.8 mol dm^{-3} $Na_2[SO_4]$ at I = 5 mol dm^{-3} was examined at 25, 47, 60, and 70 °C. Linear plots were obtained when equation (1) was applied. The results for K_1 are shown in Table 3.

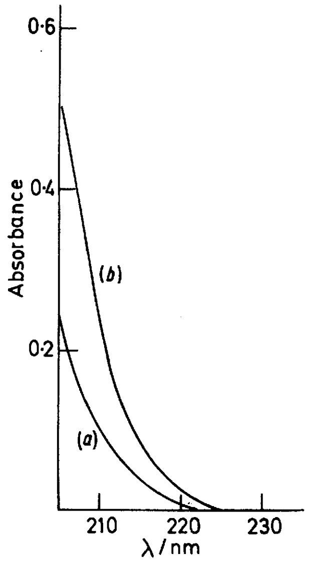

FIGURE 1 Effect of sulphate ions on the absorption spectrum of 0.1 mol dm^{-3} nickel(II) perchlorate at 25 °C and I = 5 mol dm^{-3}. $[SO_4^{2-}]$ = 0.1 (*a*) and 1.0 mol dm^{-3} (*b*)

TABLE 3

Effect of temperature on K_1 and ε_1 for $Ni[SO_4]$, and on ε_0 for $Ni[ClO_4]_2$ for I = 5 mol dm^{-3}

	47 °C			60 °C			70 °C		
λ/nm	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}
206	6.8	36.1	0.83	4.7	58	0.85	6.4	70	0.91
208				5.5	42	0.77	5.0	58	0.80
210				6.4	29	0.71	4.9	43	0.72
Mean				5.5 ± 0.3			5.4 ± 0.3		

TABLE 4

Effect of temperature on K_1, ε_1 for $Cu[SO_4]$, and ε_0 for $Cu[ClO_4]_2$ at I = 5 mol dm^{-3}

	25 °C			34 °C			47 °C			60 °C		
λ/nm	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}	K_1/dm^3 mol^{-1}	ε_1/dm^3 mol^{-1}	ε_0/cm^{-1}
235	4.0	640	140	3.8	770	160	4.6	810	160			
240	4.2	560	68	3.8	770	77	4.5	820	87	4.8	960	95
Mean *	4.2 ± 0.1			3.9 ± 0.1			4.5 ± 0.1			4.6 ± 0.1		

* From six values of λ from 235 to 270 nm.

The Copper(II)*–Sulphate System*.—A copper(II) perchlorate solution at $I = 5.0$ mol dm^{-3} has an absorbance peak at *ca.* 200 nm ($\varepsilon_0 \simeq$ 1 300 dm^3 mol^{-1} cm^{-1}). Addition of sulphate ions causes a marked increase in absorbance in the 230—300 nm region at 25 and 60 °C. An isosbestic point at 218 nm indicated the presence of two absorbing species, Cu^{2+} and $Cu[SO_4]$ (Figure 2). The use of equation (1) resulted in linear plots. The formation constants (Table 4) vary little with temperature. Literature values at I = 3.0 mol dm^{-3} are 2.4 [13] and 4.0 dm^3 mol^{-1}.[4,14]

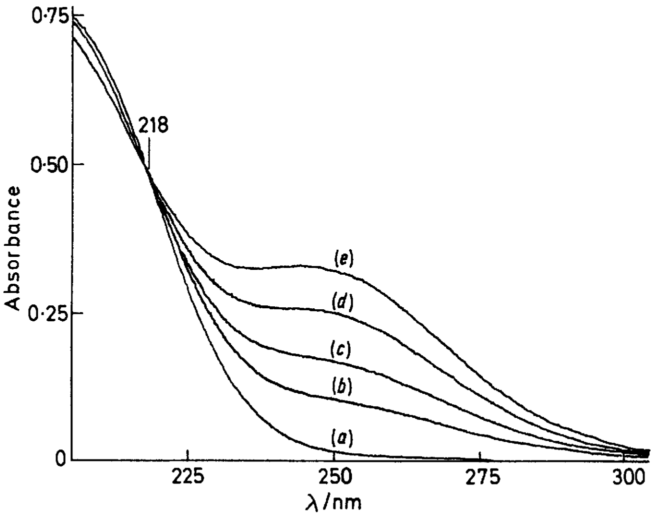

FIGURE 2 Effect of sulphate ions on the absorption spectrum of 0.0048 mol dm^{-3} copper(II) perchlorate at 60 °C and I = 5 mol dm^{-3} in 1-mm cells. $[SO_4^{2-}]$ = 0 (*a*), 0.05 (*b*), 0.1 (*c*), 0.2 (*d*), and 0.4 (*e*)

The Iron(III)*–Sulphate System*.—The sulphato-complexes of Fe^{III} could not be investigated under conditions unfavourable for the formation of $[HSO_4]^-$ because of extensive hydrolysis of Fe^{3+} in the pH 3 region. The conditions used were an equilibrium concentration of H^+ of 1.0 mol dm^{-3} at I = 5 mol dm^{-3}. Spectra of a series of iron(III) perchlorate solutions having increasing concentrations of free sulphate ions showed isosbestic points at 271 and 272 nm at 25 and 60 °C respectively, in good agreement with the results of Whiteker and Davidson [15] for a medium of

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[13] R. Nasanen, *Suomen Kem.*, 1953, **B26**, 67.

[14] R. A. Matheson, *J. Phys. Chem.*, 1965, **69**, 1537.

[15] R. A. Whiteker and N. Davidson, *J. Amer. Chem. Soc.*, 1953, **75**, 3081.

1.0 mol dm^{-3} perchloric acid at 25 °C. The solutions, containing concentrations of $HClO_4$ and $Na_2[SO_4]$ of 1.0—3.0 and 0—0.3 mol dm^{-3} respectively, were adjusted to $I = 5.0$ mol dm^{-3}. At 25 °C the absorbance at the isosbestic point was constant for concentrations of free sulphate ions of 0—4.22 × 10^{-3} mol dm^{-3}, but increased for 8.42 × 10^{-3} mol dm^{-3}. At 60 °C, the corresponding concentrations of sulphate ions were 0—2.24 × 10^{-3} and 4.21 × 10^{-3} mol dm^{-3}. The presence of a third absorbing species, $[Fe(SO_4)_2]^-$, is indicated at these high sulphate concentrations. Thus, equation (1) was applicable to the lower ranges of concentration and gave linear plots. The formation constants (Table 5) show a large dependence on temperature.

TABLE 5

Effect of temperature on K_1 and ε_1 for $[Fe(SO_4)]^+$ and on ε_0 for $Fe[ClO_4]_3$, at $I = 5$ mol dm^{-3} and $[HClO_4] = 1$ mol dm^{-3}

	25 °C			34 °C			47 °C			60 °C		
λ	K_1	ε_1	ε_0	K_1	ε_1	ε_0	K_1	ε_1	ε_0	K_1	ε_1	ε_0
nm	dm^3 mol^{-1}	dm^3 mol^{-1} cm^{-1}		dm^3 mol^{-1}	dm^3 mol^{-1} cm^{-1}		dm^3 mol^{-1}	dm^3 mol^{-1} cm^{-1}		dm^3 mol^{-1}	dm^3 mol^{-1} cm^{-1}	
310	205	2 870	62.7	255	2 740	67.6	320	2 630	80.4	430	2 580	87.2
Mean *	210 ± 3			265 ± 4			324 ± 3			432 ± 6		

* From five values of λ from 290 to 330 nm.

Hydrogensulphato-complexes.—The presence of hydrogensulphato-complexes in the systems investigated has not been considered for the following reasons. First, Davis and Smith[16] concluded from spectrophotometric measurements that the formation constant for $[Fe(HSO_4)]^{2+}$ must be less than one hundredth of that for $[Fe(SO_4)]^+$ at $I = 0.5$ mol dm^{-3}. Secondly, no evidence of hydrogensulphato-complexes could be found in the copper system under conditions favourable for their formation. The copper system was particularly suitable because the spectra were reasonably sensitive to changes in the concentration of free sulphate ions and the low susceptibility of Cu^{2+} to hydrolysis allowed low concentrations of acid, and hence low ratios of $[HSO_4^-] : [SO_4^{2-}]$, to be used. The spectrum of a solution of $Cu[ClO_4]_2$ containing 0.3 mol dm^{-3} sulphate at low acidity and low $[HSO_4^-]$ was compared with that of a similar solution of high acidity and high $[HSO_4^-]$ (Figure 3). The large decrease in absorbance that occurred concomitant with a large increase in the concentration of $[HSO_4]^-$ was consistent with a corresponding decrease in the concentration of a copper sulphate complex resulting from the reduction in the concentration of free sulphate ion from 0.3 to 0.1 mol dm^{-3} The resulting spectrum was very similar to that of a third solution having the same concentration of free sulphate at low acidity and low $[HSO_4^-]$, showing that a large change in $[HSO_4^-]$ had little effect on the free $[Cu^{2+}]$. Thus any copper(II) hydrogensulphate complex must be much weaker than the corresponding sulphate.

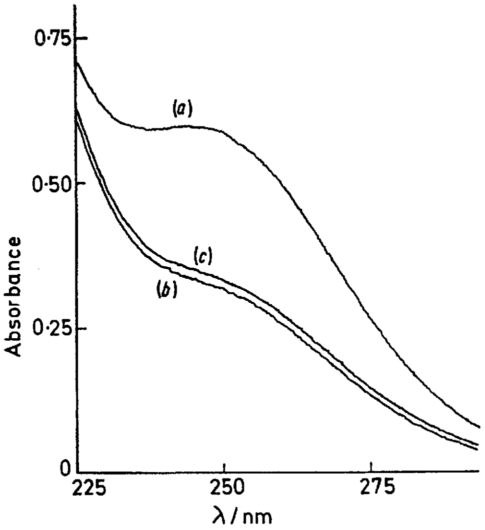

FIGURE 3 Effect of equilibrium concentrations of $[SO_4]^{2-}$ and $[HSO_4]^-$ on the absorption spectrum of 0.0048 mol dm^{-3} $Cu[ClO_4]_2$ at 60 °C and $I = 5$ mol dm^{-3} in 2-mm cells. $[SO_4^{2-}]$, $[HSO_4^-] = 0.3$, 6.17 × 10^{-4} (*a*); 0.1, 0.2 (*b*); and 0.1, 5.6 × 10^{-4} mol dm^{-3} (*c*)

The evidence for the absence of any significant contribution of hydrogensulphato-complexes in the presence of large concentrations of perchlorate ions is in accord with the similarity in charge and size of these two ions.

DISCUSSION

The thermodynamic changes involved in inner- and outer-sphere complex formation between hard acceptors and hard donors in aqueous media largely reflect the role of the solvent in the reactions. Ahrland[1] showed that the displacement of water molecules that occurs when inner-sphere complexes are formed results in higher values for $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}$ of *ca.* 20 and 25 kJ mol^{-1} respectively at 25 °C, compared with the corresponding outer-sphere values. For outer-sphere complexes, $\Delta H^{\ominus}$ values are generally small and often approach 0 since there are only minor contributions from dehydration and bond energies.[1] Conversely, moderate entropy terms can be expected when ligands having strong solvent-ordering properties such as sulphate and fluoride ions form outer-sphere complexes because of their partial dehydration. As the ionic strength increases, the presence of other ions must reduce the solvent ordering, and lower entropy terms are expected.

Inner-sphere complexes have higher $\Delta H^{\ominus}$ values compared with their outer-sphere counterparts because the negative $\Delta H^{\ominus}$ contribution from bond formation is more than offset by the increased dehydration energy that is involved.[1] This increased dehydration also leads to higher entropy terms. At infinite dilution, values of $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}$ for the sulphato-complex of Fe^{III} exceed those for that of La^{III}, and $\Delta H^{\ominus}$ and $T\Delta S^{\ominus}$ for the uranyl complex exceed those for Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} by amounts that approach the criteria, indicat-

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[16] G. G. Davis and W. M. Smith, *Canad. J. Chem.*, 1962, **40**, 1836.

ing that only $[Fe(SO_4)]^+$ and $[UO_2(SO_4)]$ are predominantly inner sphere (Table 6).[11,17-21]

TABLE 6

Thermodynamic data (kJ mol^{-1}) for monosulphato-complexes at 25 °C and $I = 0$

Metal ion	log K_1	$\Delta G^\ominus$	$\Delta H^\ominus$	$T\Delta S^\ominus$	Ref.
Fe^{3+}	4.2	−23.7	25.9	48.6	17
La^{3+}	3.50	−20.0	13.6	33.7	18
UO_2^{2+}	3.14	−17.9	21 3	39.2	19
Cu^{2+}	2.33[20]	−13.3	9.7[21]	23.0	
Ni^{2+}	2.32[11]	−13.2	5.93[21]	19.1	
Co^{2+}	2.35[11]	−13.4	6.36[21]	19.8	
Mn^{2+}	2.26[11]	−12.9	8.61[21]	21.5	

The slightly higher values of $\Delta H^\ominus$ and $T\Delta S^\ominus$ for Cu^{II} compared with the other bivalent ions also suggest some inner-sphere contribution. The position with La^{III} is much less clear, since the more positive $\Delta H^\ominus$ might be taken to indicate some inner-sphere contribution when compared with $\Delta H^\ominus$ for the bivalent ions, but, as pointed out by a referee, one cannot *a priori* expect $\Delta H^\ominus$ for the formation of an outer-sphere complex with a trivalent ion to be similar to that with a bivalent ion.

These classifications of the complexes at infinite dilution can be rationalised, and the mode of bonding of the sulphate ligand assessed as uni- or bi-dentate, by use of linear free-energy relations (l.f.e.r.s) involving oxygen-donor ligands that are known to be uni- (acetate), bi- (oxalate), or tri-dentate (citrate). It has been shown[22] that log K_1 values for oxalato- and acetato-complexes are related by equation (2) where n is the number of

$$\log K_1(\text{oxalate}) = f \log K_1(\text{acetate}) + (n-1)\log 55.5 \quad (2)$$

co-ordinated groups on the ligand, f is a factor that takes into account steric hindrance and electrostatic repulsion between the charged donor atoms in the oxalate ligand, and $(n-1)\log 55.5$ arises from Adamson's proposal[23] regarding the asymmetry of the standard state. Figure 4 demonstrates that there is also an l.f.e.r. between log K_1(acetate) and log $K_1(OH^-)$ for a wide variety of metal ions. Similar relations are found for other $[OR]^-$ ligands. Thus, equation (2) becomes, in the general case, (3) for ligands having n negatively charged

$$\log K_1(L) = f \log K_1(OH^-) + (n-1)\log 55.5 \quad (3)$$

oxygen atoms. Thus, plots of log $K_1(L)$ for an n-dentate ligand against log $K_1(OH^-)$ for a variety of metal ions should yield intercepts of $(n-1)\log 55.5$.

Figure 4 shows that straight lines can be drawn through the points having high values of log $K_1(OH^-)$ for acetate, oxalate, and citrate ligands. The expected intercepts of 0, 1.74 (= log 55.5), and 3.48 (= 2log 55.5) were obtained for values of n of 1, 2, and 3 respectively. As lower values of log $K_1(OH^-)$ are approached, values of log $K_1(L)$ for acetates become higher than those expected from the straight line, and hence show a larger intercept than 0. This deviation must represent the contribution from the outer-sphere complex. The intercepts (broken lines) correspond to values of log K_1 calculated from the Fuoss[24] equation for the charge products −2, −4, and −6, for the various metal ions and ligands,[25,26] assuming these to refer to the outer-sphere constants, log K_1^{out}; K_1^{in} and K_1^{out} are defined in ref. 26. A centre-to-centre distance of $a = 4.5$ Å was used for the calculation of log K_1^{out} because this gave the most reasonable values, although the calculated value of log K_1^{out} is relatively insensitive to a for charge products less negative than −6, so that the interpretation of Figure 4 is not dependent on the selection of a value for a. The dotted line corresponds to log $(K_1^{in} + K_1^{out})$ for the acetato-complexes of metal ions with a charge product of −2, where log K_1^{in} is obtained from the extrapolation of the straight line for log K_1(acetate), and log K_1^{out} is the Fuoss value. log K_1 [= log $(K_1^{in} + K_1^{out})$] cannot be less than the Fuoss value, and must approach this value as the inner-sphere attraction becomes less. Thus, the acetato-complexes of Mn^{II}, Mg^{II}, Ca^{II}, Sr^{II}, and Ba^{II} appear to contain increasing proportions of an outer-sphere complex in that order.

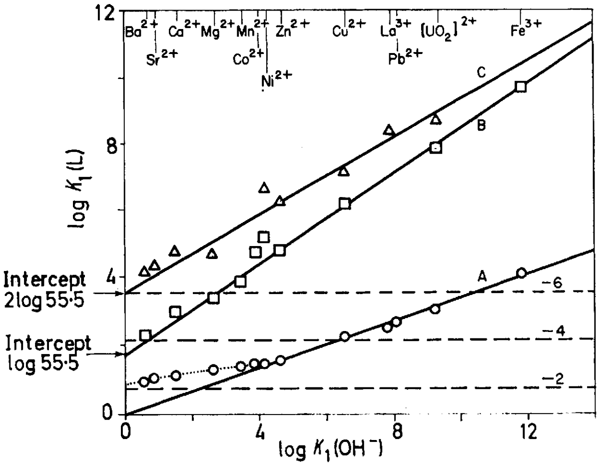

FIGURE 4 Linear free-energy relation of log K_1 values at infinite dilution and 25 °C for the formation of acetato- (○), oxalato- (□), and citrato-complexes (△) against those for the corresponding hydroxo-complexes. (— — —) log K_1(L) calculated from the Fuoss[24] equation for the ionic charge product indicated. Acetate values for Fe^{3+} and $[UO_2]^{2+}$ (ref. 25) and all other values[26] were corrected to $I = 0$ by the Davies equation where necessary

A similar situation is found for the sulphato-complexes. The bivalent metal-ion complexes that have been classified as outer sphere from thermodynamic values and absorption spectra lie on the broken line as expected

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[17] R. L. S. Willix, *Trans. Faraday Soc.*, 1963, **59**, 1315.

[18] R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, *J. Chem. Soc.* (*A*), 1969, 47.

[19] R. M. Wallace, *J. Phys. Chem.*, 1967, **71**, 1271.

[20] W. D. Bale, E. W. Davies, and C. B. Monk, *Trans. Faraday Soc.*, 1956, **52**, 816.

[21] H. K. J. Powell, *J.C.S. Dalton*, 1973, 1947.

[22] R. D. Hancock and F. Marsicano, *J.C.S. Dalton*, 1976, 1096.

[23] A. W. Adamson, *J. Amer. Chem. Soc.*, 1954, **76**, 1578.

[24] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

[25] D. W. Archer and C. B. Monk, *J. Chem. Soc.*, 1964, 3117.

[26] 'Stability Constants of Metal–Ion Complexes,' *Special Publ.*, The Chemical Society, London, 1964 (no. 17) and 1971 (no. 25).

(Figure 5). Evidence from both i.r. spectroscopy [27] and ultrasonic measurements [28] agrees with this classification. The $[Fe(SO_4)]^+$ and $[UO_2(SO_4)]$ complexes, which appear from Table 6 to be inner sphere, lie on the appropriate line. The complex $[In(SO_4)]^+$ appears to be a mixture of inner and outer sphere from Figure 5, in agreement with the i.r. spectrum which suggests 50% inner sphere. The complex $[La(SO_4)]^+$ appears to be predominantly outer sphere from the position close to the broken line for charge product −6. This is in agreement with the i.r. evidence,[27] which suggests 12% inner sphere for Ce^{III} which can be expected to be closely similar to La^{III}, but does not support the ultrasonic measurements [29] which suggest 79% inner sphere. As mentioned above, $\log K_1^{out}$ for charge product −6 is sensitive to a so that one might suggest that our assumption of constant a has broken down for the large La^{III}. If we accept that the lanthanum(III) sulphate complex is 79% outer sphere, this allows us to calculate $\log K_1^{out}$ 2.80 from $\log K_1(SO_4^{2-})$ 3.50. To generate $\log K_1^{out}$ 2.80 from a charge product of −6 would require an a value of >6 Å which seems too large in relation to the value of 4.5 Å which produces satisfactory results for the other metal ions. At this stage we prefer the indications of Figure 5 (coupled with the evidence from i.r.) that the lanthanum(III) sulphate complex is predominantly outer sphere {and that the thermodynamics of formation of $[La(SO_4)]^+$ should be interpreted accordingly} to the ultrasonic evidence which suggests that it is predominantly inner sphere.

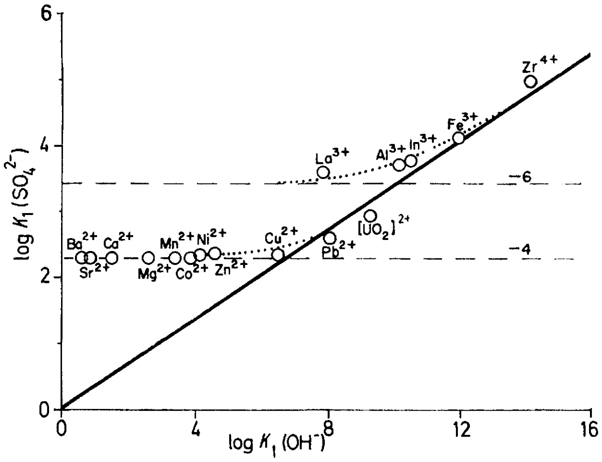

FIGURE 5 Linear free-energy relation of $\log K_1$ values at infinite dilution and 25 °C for the formation of sulphato-complexes against those for the corresponding hydroxo-complexes. All the values were taken from ref. 27 and corrected to $I = 0$ by use of the Davies equation where necessary. (— — —) $\log K_1(L)$ calculated from the Fuoss [24] equation for the ionic charge product indicated

The question of whether $[SO_4]^{2-}$ behaves as a uni- or bi-dentate ligand can be answered tentatively by reference to Figure 5. Extrapolation of the line joining the values for the inner-sphere complexes cannot have an intercept much above 0, so that the mode of bonding of the sulphate ion to the metal ions in these inner-sphere complexes appears to be unidentate.

At high ionic strength the classification of the complexes remains unchanged, although large decreases in $T\Delta S^{\ominus}$ (15—20 kJ mol^{-1}) and smaller decreases in $\Delta H^{\ominus}$ (5—9 kJ mol^{-1}) occur for both inner- and outer-sphere complexes, compared with an ionic strength of 0 (Tables 6 and 7). The reduced entropy changes can be attributed to the smaller effect of the metal ion and ligand on the solvent structure that results from the presence of the background electrolyte, and the decrease in ΔH is consistent with the reduced hydration of the ions expected at high ionic strength. The same features occur for the reaction $H^+ + [SO_4]^{2-} \longrightarrow [HSO_4]^-$, with decreases of *ca.* 13 kJ mol^{-1} in $T\Delta S^{\ominus}$ and 10 kJ mol^{-1} in $\Delta H^{\ominus}$ when I increases from 0 to 5 mol dm^{-3} (Table 1). A similar trend in the entropy term has been reported by Ahrland [1] for a change in I from 0 to 2 mol dm^{-3}, with $T\Delta S^{\ominus}$ decreasing by 8.3 kJ mol^{-1} for $[Cu(SO_4)]$.

TABLE 7

Thermodynamic values (kJ mol^{-1}) for monosulphato-complexes at 25 °C and $I = 5$ mol dm^{-3}

Metal ion	log K_1	$\Delta G^{\ominus}$	$\Delta H^{\ominus}$	$T\Delta S^{\ominus}$
Fe^{3+}	2.32	−13.2	16.4	29.6
Ni^{2+}	0.77	−4.4	0	4.4
Cu^{2+}	0.63	−3.6	0	3.6

Evidence for the classification of the complexes provided by their absorption spectra at $I = 5$ mol dm^{-3} is generally consistent with the thermodynamic values. Thus, the high value of the absorption coefficient of the $[Fe(SO_4)]^+$ complex in the u.v. (Table 8) is characteristic of a c.t. band. The thermodynamic values clearly indicate an inner-sphere complex, which must, therefore, give rise to the band in this instance. The slight change in absorbance of the band at 520 nm of $Co[ClO_4]_2$ in the presence of sulphate at 25 °C was indicative of a very weak inner-sphere complex. Both the position of this band, and the absorption coefficient at 50 °C, a temperature suitable for measurement of the complex characteristics, confirm an inner-sphere structure (Table 8). This conclusion is consistent with the view that the complex is predominantly outer-sphere at 25 °C.[4]

TABLE 8

Characteristics of the absorption band for monosulphato-complexes at $I = 5$ mol dm^{-4}

Metal ion	λ / nm	ε_1 / dm^3 mol^{-1} cm^{-1}	θ_c / °C
Fe^{3+}	310	2 900	25
Co^{2+}	520	5.4	50
Ni^{2+}	206	36	47
Cu^{2+}	235	640	25

An outer-sphere configuration for $[Ni(SO_4)]$ is indicated by the position of the absorption band in the far u.v., but the low absorption coefficients are in the range expected for an inner-sphere structure. However, the rapid increase in absorption coefficient with decreas-

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[27] R. Larsson, *Acta Chem. Scand.*, 1964, **18**, 1923.

[28] M. Eigen and K. Tamm, *Z. Elektrochem.*, 1962, **66**, 93, 107.

[29] D. P. Fay, D. Litchinsky, and N. Purdie, *J. Phys. Chem.*, 1969, **73**, 544.

ing wavelength (Table 3) means that the absorption at the peak could increase considerably to the magnitude expected for outer-sphere configurations. Measurements could not be made at such low wavelengths. The failure of sulphate ions to modify the visible spectrum of nickel(II) perchlorate supports the evidence for an outer-sphere complex gained from the u.v. spectra and thermodynamic values.

The $[Cu(SO_4)]$ complex is classified as predominantly outer sphere, both from the position of the absorption band that has a peak in the far u.v. and from the intensity. Although the absorption coefficient approaches 1 000 $dm^3 mol^{-1} cm^{-1}$ only at high temperature and ionic strength, there is little doubt that this is a weak c.t. band. The outer-sphere configuration is consistent with the results of Mironov *et al.*[4] who obtained a value of 0.3 $dm^3 mol^{-1}$ for the formation constant of the inner-sphere complex, compared with 4.7 $dm^3 mol^{-1}$ for the outer-sphere species, and also agrees with the thermodynamic evidence.

EXPERIMENTAL

Materials and Solutions.—AnalaR-grade materials were used, unless otherwise stated. Sulphuric acid and sodium sulphate provided the required concentrations of H^+, $[HSO_4]^-$, and $[SO_4]^{2-}$. Constant ionic strength was maintained with sodium perchlorate. Stock solutions of the perchlorates of Mn^{II}, Fe^{II}, and Co^{II} in 10^{-2} mol dm^{-3} perchloric acid were prepared from the hexahydrate salts (G. F. Smith Chemical Company). The presence of a slight iron(III) content in the iron(II) solid was indicated by an absorption band at 340 nm due to $[FeCl]^{2+}$ that appeared on addition of sodium chloride. The impurity was reduced to Fe^{II} by the addition of small amounts of iron sponge (Specpure grade; Johnson, Matthey Chemicals Ltd.) to a solution that had been deoxygenated by nitrogen. The excess of iron sponge was removed by filtration shortly before use.

Stock solutions of the perchlorates of nickel and copper were prepared by dissolution of $Ni[CO_3]$, $2Ni[OH]_2 \cdot 4H_2O$ (B.D.H., laboratory reagent low in cobalt and iron), and $Cu[CO_3] \cdot Cu[OH]_2 \cdot H_2O$ (B.D.H. laboratory reagent) in a slight excess of $HClO_4$. Iron(III) perchlorate solution prepared by dissolution of Specpure iron sponge in $HClO_4$, followed by oxidation of Fe^{II} to Fe^{III} with hydrogen peroxide, contained enough chloride for the absorption of $[FeCl]^{2+}$ at 340 nm to interfere. The chloride was probably formed from slight reduction of the perchlorate ion by Fe^{II}. A satisfactory product was obtained by the dissolution of iron(III) nitrate in $HClO_4$ and precipitation of iron(III) hydroxide with sodium hydroxide. The filtered precipitate was washed clear of chloride and dissolved in $HClO_4$.

Spectra were recorded on a Beckman Acta III spectrophotometer fitted with temperature-controlled cell holders suitable for cells having pathlengths of 0.1—1.0 cm.

Determination of the Hydrogensulphate Formation Constant.—Undissociated picric acid is colourless but dissociates to form the highly coloured picrate ion. By comparison of the absorbance of a picric acid solution containing known added concentrations of acid and sulphate ions with that of a calibration curve for picric acid solutions of known acid strength in the absence of sulphate ions, the concentration of free hydrogen ions was obtained. All the measurements were made at the absorbance peak at 358 nm in solutions of $I = 5.0$ mol dm^{-3}. A stock solution of picric acid in water (*ca.* 0.002 mol dm^{-3}, 5 cm^3) was added to a flask (50 cm^3) and the other components were added. The concentrations of $HClO_4$ and $Na_2[SO_4]$ were in the ranges 0.0382—0.23 and 0.0283—0.25 mol dm^{-3} respectively. Several solutions were examined at 25, 34, 47, and 60 °C. The results calculated from the calibration curves were as follows:

$\frac{\theta_c}{°C}$	$\frac{K_1}{dm^3 mol^{-1}}$
25.0	34.3 ± 1.5
34.0	39.1 ± 1.7
47.0	49.0 ± 1.9
60.0	62.0 ± 2.0

We thank Miss A. J. Bembridge for assistance, and the Director General of the National Institute for Metallurgy for permission to publish this work.

[6/1857 *Received, 4th October,* 1976]