Entropy Titrations: A Reassessment of Data for the Reaction of the Sulphate Ion with Trivalent Lanthanoid Ions

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The simultaneous determination of log K° and ΔH° for anion–cation interactions is examined with reference to the reactions $M^{3+} + SO_4^{2-} \rightleftharpoons MSO_4^{+}$ and $MSO_4^{+} + SO_4^{2-} \rightleftharpoons M(SO_4)_2^{-}$ (M = lanthanoid). Limitations of the 'entropy titration' approach are outlined. From published enthalpimetric data ΔH° values for the formation of the monosulphate ion pairs have been recalculated using published K° data. For the formation of the bis(sulphate) ion pair ΔH° and K° have been recalculated from enthalpimetric data by graphical methods and by general non-linear least-squares analysis.

THE entropy titration method for simultaneous determination of K° and ΔH° from enthalpimetric titrations has received wide application since its introduction by Becker *et al.*[1] We [2] and others [3,4] have pointed to the limitations of this method. In a recent publication [2] we criticised the application of this method to the reaction of the sulphate ion with protons and with bivalent metal ions [5-7] and drew attention to (i) the inadequacy of iterative methods,[3,5-7] rather than general non-linear least-squares methods, for simultaneous calculation of parameters from the experimental data; (ii) the dependence of the results on the relationships assumed in the minimisation of residuals; (iii) the profound effect of the

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[5] J. J. Christensen, R. M. Izatt, L. D. Hansen, and J. A. Partridge, *J. Phys. Chem.*, 1966, **70**, 2003.

[6] R. M. Izatt, D. Eatough, J. J. Christensen, and C. H. Bartholomew, *J. Chem. Soc.* (*A*), 1969, 45.

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

chosen activity coefficient expression on the computed K° and ΔH° for ion-pairing reactions; and (iv) the greater reliability of employing potentiometrically determined K° data to calculate ΔH° from calorimetric measurements for these reactions.

In this paper we focus attention on the reaction of the sulphate ion with trivalent lanthanoid ions and (i) discuss the effect of the choice of activity coefficient relationship, and of a°, the assumed distance of closest approach of the ions, on the calculated value of ΔH°; (ii) discuss evidence for the existence of both 1 : 1 and 2 : 1 sulphate–lanthanoid ion pairs; (iii) recalculate $\Delta H_1{}^\circ$ for reaction (1) from published (conductometric) $K_1{}^\circ$ data and calorimetric enthalpy data; and (iv) recalculate $K_2{}^\circ$ and $\Delta H_2{}^\circ$ for reaction (2) by application of both general non-linear least-squares and graphical methods to enthalpimetric data.

$$M^{3+} + SO_4{}^{2-} \rightleftharpoons MSO_4{}^{+} \qquad (1)$$

$$MSO_4{}^{+} + SO_4{}^{2-} \rightleftharpoons M(SO_4)_2{}^{-} \qquad (2)$$

A complete non-linear least-squares analysis to determine the four parameters $K_1{}^\circ$, $K_2{}^\circ$, $\Delta H_1{}^\circ$, and $\Delta H_2{}^\circ$ from enthalpimetric data could not be achieved; the computation was non-convergent, as was the case for bivalent metal sulphates.[2]

1 : 1 *Lanthanoid–Sulphate Ion Pairs.*—Izatt *et al.*[7] have calculated $K_1{}^\circ$ and $\Delta H_1{}^\circ$ (and $K_2{}^\circ$ and $\Delta H_2{}^\circ$) from calorimetric data[8] for the titration of $0{\cdot}5005\text{M}$-$(Me_4N)_2SO_4$ into acidic solutions of lanthanoid perchlorates (*ca.* 0·02M, pH *ca.* 2·0—3·5). Activity coefficients were calculated from equation (3), $B = 0{\cdot}329$ Å, assuming $a^\circ = 5{\cdot}0$ Å and $\beta = 0{\cdot}5$. Calculations involved the iterative 'entropy titration' procedure which varied

$$\log \gamma_\pm = -AZ^2 \left\{ \frac{\sqrt{I}}{1 + Ba^\circ\sqrt{I}} - \beta I \right\} \qquad (3)$$

one parameter, $K_1{}^\circ$, calculated the value of the other parameter ΔH at each data point, and calculated the average value of this parameter through the data set ($\overline{\Delta H}$); the 'best pair' of parameters $K_1{}^\circ$, $\overline{\Delta H}$ were those which gave a minimum in the error square sum [ref. 2, equations (4)—(6)]. However, as only the one parameter $K_1{}^\circ$ was varied, $\overline{\Delta H}$ is a function of $K_1{}^\circ$, whereas both K and ΔH should be varied independently[2] (as in a general non-linear least-squares calculation) to obtain a correct minimum in the error square sum.[9] Also no allowance was made for the dependence of ΔH on ionic strength, so the derived enthalpy change $\overline{\Delta H}$ (though reported[7] as ΔH°) is the average value of the concentration-dependent molar enthalpy change (and differs from ΔH° by *ca.* 3 kJ mol^{-1} in the ionic strength range concerned, *ca.* 0·1M). Further, as pointed out by Fay and Purdie,[10] the calculated value of ΔH is rather insensitive to the value chosen for $K_1{}^\circ$ (since $K_1{}^\circ$ is very large, *ca.* 4×10^3); they suggest that a 30% change in $K_1{}^\circ$ causes less than 1% change in ΔH [although our calculations show that a 10% (or 20%) decrease in $K_1{}^\circ$ effects a 2% (or 3%) increase in ΔH°]. This lack of sensitivity would not aid an analysis by iterative calculation.

Fay and Purdie[10] made a calorimetric study of the formation of 1 : 1 lanthanoid–sulphate ion pairs by titrating a sodium sulphate solution into a solution containing a large molar excess of lanthanoid nitrate. $\overline{\Delta H}$ was calculated by use of Spedding and Jaffe's[11] (conductometric) stability constants $K_1{}^\circ$, although a different equation for activity coefficients was used [equation (4), $a^\circ = 8{\cdot}86$ Å]. No attempt was made to

$$\log \gamma_\pm = -AZ^2 \left\{ \frac{\sqrt{I}}{1 + 2{\cdot}92\sqrt{I}} - 0{\cdot}3I \right\} \qquad (4)$$

correct $\overline{\Delta H}$ (I *ca.* 0·3M) to $\Delta H_1{}^\circ$ ($I = 0$).

The derived values for K° and ΔH° are critically dependent on the expression chosen for the ionic activity coefficients.[2,12,13] The different values of a° used by Izatt *et al.* and Fay and Purdie approximate to the formation of contact, MSO_4, and solvent separated, $M(H_2O)_2SO_4$, ion pairs respectively; relaxation spectrometry studies[14] on the rate of formation of lanthanoid monosulphates have indicated that these species exist predominantly (79—93%) as contact ion pairs.

The value of a° for a contact ion pair may be approximated to the sum of the ionic radius of the lanthanoid ion (average 1·12 Å) and the thermochemical radius[15] for the sulphate ion (2·30 Å), *viz* 3·42 Å. [This figure can be compared with (a) the sum of the radii of the solvated ions (3·95 + 2·29 Å) as derived from ionic mobilities in H_2O,[16] or (b) the sum of the radii of the ions (3·42 Å) plus the diameter of a water molecule[17] (2·92 Å), *viz.* 6·34 Å.] The Davies equation[18] [equation (3) with $\beta = 0{\cdot}2$ or 0·3 and with $a^\circ = 3{\cdot}04$ Å] has been found to be satisfactory in predicting the activity coefficients for (i) lanthanum bromide solutions,[19] (ii) ion-pairing lanthanum and lutetium malonates,[20] (iii) lanthanum sulphate,[21,22] and (iv) ytterbium sulphate.[23,24] In contrast Newton

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[8] Data supplementary to ref. 7; document No. 00185 obtained from ASIS National Auxiliary Publication Service, c/o CCM Information Services, 22 West 34th Street, New York, 10001.

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[11] F. H. Spedding and S. Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 882.

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[13] A. K. Covington, J. V. Dobson, and K. V. Srinivasan, *J.C.S. Faraday I*, 1973, 94.

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and Arcand,[25] using the Debye–Hückel equation, derived values of $a° = 6{\cdot}57$ from a study on the solubility of cerium sulphate in potassium sulphate solution ($I = 0{\cdot}02$—$0{\cdot}3$M) and $a° = 5{\cdot}73$ Å from a spectrophotometric analysis of $CeSO_4^+$ ion pair formation in sodium perchlorate solutions.

In reassessing the calorimetric data of Izatt *et al.*[7,8] we have used the $K_1°$ values published by Spedding and Jaffe [11] (with interpolated values [10] for Eu, Tb, Dy, Tm, and Lu); this is the most comprehensive set of $K_1°$ values available and, where comparison is possible, they are in general agreement with values published by other workers.[26] These values are based on conductivity measurements over a very wide range of ionic strengths ($I < 0{\cdot}003$ to $>0{\cdot}60$); $K_1°$ was calculated from the derived concentration quotients K_1 [equation (5)] by use of a Debye–Hückel expression for mean ionic activity coefficients for $M_2(SO_4)_3$, $\gamma_{2.3\pm}$, and $(MSO_4)_2SO_4$, $\gamma_{1.2\pm}$ [equation (6)]. All 36 enthalpimetric data points were used for each metal ion. Molar concentrations could be used because of the small temperature changes involved in the calorimetric measurements (max. 0·08 °C).

TABLE 1

Thermodynamic data for the reactions $M^{3+} + SO_4^{2-} \rightleftharpoons MSO_4^+(aq)$ at 25 °C

		M^{3+}											
		La	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$K_1°$ (±10%)/l mol^{-1} [a]		4170	4170	4350	4550 [b]	4550	4320 [b]	4080 [b]	3850	3850	3850 [b]	3850	3850
$\Delta H_1°$ (±0·4)/kJ mol^{-1} (Spedding–Jaffe activities)		18·4$_5$	19·8$_5$	20·0	20·5$_5$	19·9$_5$	19·7	20·3$_5$	20·4	20·3	20·0	19·8	(19·5) [c]
$\overline{\Delta H_1}$/kJ mol^{-1} (Ref. 7, $I = 0{\cdot}1$M)		13·6	14·6	15·1$_5$	15·2$_5$	15·0	15·0$_5$	15·4$_5$	15·3	15·1	15·0$_5$	15·0$_5$	13·7$_5$
$\overline{\Delta H_1}$/kJ mol^{-1} (Ref. 10, $I = 0{\cdot}3$M)		13·1 [d]	16·4	17·4	17·3	17·1$_5$	15·5 [d]	15·0	14·8	14·1 [d]	13·2	12·1	14·8
$\Delta H_1°$ (±3%)/kJ mol^{-1} Equation (3), β = 0·3	$a° = 3{\cdot}04$	20·0	21·6	21·8	22·5	21·5	21·2	22·2	22·2	22·0	21·6	21·4	20·7
	$a° = 3{\cdot}42$	19·4	21·0	21·2	21·8	20·9	20·6	21·5	21·5	21·3	20·9	20·8	20·1
	$a° = 5{\cdot}0$	17·6	19·1	19·2	19·8	19·1	18·7	19·5	19·4	19·2	18·9	18·7	18·1
	$a° = 6{\cdot}0$	17·0	18·4	18·5	19·1	18·4	18·0	18·8	18·7	18·5	18·1	18·0	17·5
	$a° = 8{\cdot}0$	16·0	17·4	17·6	18·1	17·4	17·0	17·8	17·6	17·5	17·1	17·0	16·5
	$a° = 9{\cdot}26$	15·4											

[a] Ref. 11. [b] Interpolated values, ref. 10. [c] Average; values ranging 20·0—19·1—19·9 through data set. [d] Redetermined values; N. Purdie, personal communication.

$$K_1° = \frac{[MSO_4^+]}{[M^{3+}][SO_4^{2-}]} \cdot \frac{(\gamma_{1.2\pm})^{\frac{3}{2}}}{(\gamma_{2.3\pm})^{\frac{5}{2}}} \qquad (5)$$

$$-\log \gamma_{ij\pm} = A|Z_iZ_j|\sqrt{I}(1 + 0{\cdot}329a°\sqrt{I}) \qquad (6)$$

An iterative procedure was used to calculate the solution composition at each titration point. From an approximate value of the ionic strength I, the activity coefficient expressions $(\gamma_{1,2\pm})^{\frac{3}{2}}/(\gamma_{2.3\pm})^{\frac{5}{2}}$ and $\gamma_{HSO_4}/\gamma_H\gamma_{SO_4}$ (Davies equation, β = 0·3) were calculated and these were used to obtain values for the concentration quotients K_{MSO_4} and K_{HSO_4} from the respective thermodynamic equilibrium constants. The solution composition was then calculated by use of the mass balance equations for T_M, T_{SO_4}, and T_H; an improved value of I was then obtained and the process was repeated until convergence (to ±0·1%) was achieved for both [H^+] and [SO_4^{2-}]. Convergence was achieved in 3—7 cycles. With reference to the computed ionic strength, Q_{obs} was then corrected for the heat of dilution of the 0·5005M-$(Me_4N)_2SO_4$ titrant,[7] for the protonation of the sulphate ion,[2] and for the formation of the ion pair $Me_4N^+ClO_4^-$.[6] ΔH was calculated from Q_{corr} and [MSO_4^+], and $\Delta H°$ was calculated from the expression (7) by use of equations (15) ($a° = 5{\cdot}0$ Å), (16), and (17) in ref. 2 (Q' *ca.* 3·0—3·1 kJ mol^{-1}).

$$\Delta H° = \Delta H + Q' = \Delta H + RT^2\Sigma\left[\frac{n_s\partial \ln f_s}{\partial T}\right]_p \qquad (7)$$

For the lanthanoids La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb, $\Delta H_1°$(calc) was approximately constant (± <0·15 kJ mol^{-1}) up to the sixteenth data point, at which the ratio of $T_{SO_4} : T_M$ in solution is *ca.* 0·70—0·75. $\Delta H_1°$(calc) then increased linearly with increasing sulphate ion concentration (Figure) and the form of this curve is taken to indicate the presence of at least two species in solution, with the 1 : 1 species MSO_4^+ predominating at low sulphate ion concentrations. The value of $\Delta H_1°$ was determined as the limiting value of $\Delta H_1°$(calc) as $[SO_4^{2-}] \longrightarrow 0$. $\Delta H_1°$ Values are given in Table 1, and are compared with those values reported by Izatt *et al.*[7] and Fay and Purdie [10] [both of which are $\overline{\Delta H}$ values and should be compared with ΔH_1 ($\sim\Delta H_1° - 3{\cdot}0$ kJ mol^{-1})]. The uncertainties in $\Delta H_1°$ were determined by varying $K_1°$ by ±10%.[11] [In the case of Ce and Sm $\Delta H_1°$(calc) increased almost uniformly through the data set, with a very minor inflexion at the sixteenth data point; no further analysis of these data was attempted.]

For comparison the data were also analysed using equation (3) for activity coefficients with β = 0·3 and values of $a°$ in the range 3·04—9·26 Å. For each metal ion $\Delta H_1°$(calc) decreased with increasing values of

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[25] T. W. Newton and G. M. Arcand, *J. Amer. Chem. Soc.*, 1953, **75**, 2449.

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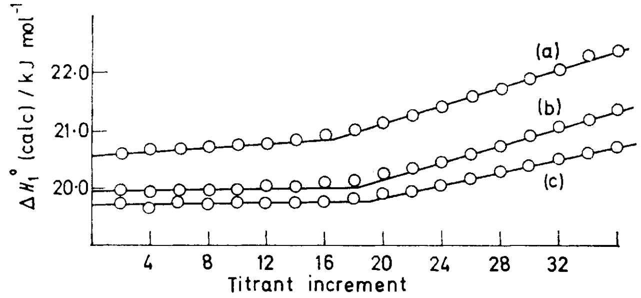
a°; for each a° ΔH_1°(calc) spanned a range of *ca.* 1 kJ mol^{-1}, with a minimum near the centre of the data set. These results do not afford evidence for the existence of either one or two ion pair species in solution and suggest an inappropriate choice either of activity coefficient expression or of a°. The critical dependence of ΔH_1° on the value of a° relates to the high charges on the reactant species.[2] Table 1 records the average values of ΔH_1°.

1 : 2 *Lanthanoid-Sulphate Ion Pairs.*—The results summarised in the Figure afford evidence for the existence at high sulphate concentrations of an ion pair with SO_4^{2-} : M^{3+} stoicheiometry >1 : 1. Charvalho and Choppin[27] deduced the existence of the species $M(SO_4)_2^-$ from potentiometric measurements (2M-$NaClO_4$), whereas Archer and Monk[23] found no evidence for a $Yb(SO_4)_2^-$ complex from ion exchange studies. Izatt *et al.*[7] postulated the existence of $M(SO_4)_2^-$ species on the basis of a decrease in the error square sum when this species was included in a least-squares analysis; however such evidence cannot be considered to establish the existence of a second ion pair.



Plot of ΔH_1°(calc) against titration increment for the enthalpimetric titration of $(Me_4)_2SO_4$ into lanthanoid perchlorate solutions; (a) Eu, (b) Gd, (c) Tb

We have analysed the data in terms of the stepwise formation of the ion pairs MSO_4^+ and $M(SO_4)_2^-$. The two parameters K_2° and ΔH_2° were simultaneously determined by use of (a) the graphical method of Bolles and Drago,[28] and (b) a general non-linear least-squares calculation.

(a) *Graphical method.* Equations (8) and (9) relate the concentration quotient K_2, the constant K_2°, and ΔH for the formation of $M(SO_4)_2^-$. For the correct

$$K_2 = K_2^\circ \cdot \frac{\gamma_{MSO_4}\gamma_{SO_4}}{\gamma_{M(SO_4)_2}} = \frac{\dfrac{Q_{obs}}{\Delta H} \cdot \dfrac{1000}{V(\text{ml})}}{[MSO_4^+][SO_4^{2-}]} \qquad (8)$$

$$\Delta H_2^\circ = \Delta H_2 + Q' = \frac{1000 Q_{obs} \text{fn}(\gamma)}{K_2^\circ V [MSO_4^+][SO_4^{2-}]} \qquad (9)$$

value of K_2° all experimental data will give the correct value of ΔH_2° from equation (9). However, for each data point a plot of ΔH_2°(calc) against $(K_2^\circ)^{-1}$ for a series of ' chosen ' K_2° in the region of the ' correct ' K_2° will give a straight line. These lines will intercept in a graphical area defined by (K_2° ± error), (ΔH_2° ± error).

The solution composition at each titration point was calculated by an iterative procedure. From an approximate value for the ionic strength I, activity coefficients were calculated [using equation (3) to calculate $\gamma_{M(SO_4)_2}/\gamma_{MSO_4}\gamma_{SO_4}$; $\beta = 0{\cdot}3$, $a^\circ = 5{\cdot}0$ Å] and these were used to calculate the concentration quotients $K_{M(SO_4)_2}$, K_{MSO_4}, and K_{HSO_4}. A cubic expression for the equilibrium sulphate ion concentration was derived from the mass balance equations for T_M, T_{SO_4}, and T_H; the expression was solved by the Newton Rapson[29] method, convergence being achieved to $\pm 0{\cdot}5\%$ in 3 cycles. An improved value of the ionic strength was derived and the process was repeated until the ionic strength was invariant ($\pm 0{\cdot}1\%$; 1—3 cycles).

With reference to the derived ionic strength, the infinite dilution correction terms ($Q_i' = \Delta H_i^\circ = \Delta H_i$) were calculated using equation (7) ($Q_1' \sim 3{\cdot}0$ kJ mol^{-1}, $Q_2' \sim 1{\cdot}0$ kJ mol^{-1}), and Q_{obs} was corrected for the heat of dilution of titrant, for the protonation of sulphate ion, for the formation of the ion pair $Me_4N^+ClO_4^-$, and for the formation of MSO_4^+ $\{Q_{MSO_4} = (\Delta H_1^\circ - Q_1')V\text{-}([MSO_4^+] + [M(SO_4)_2^-])\}$. ΔH_2° was calculated from equation (10). From the first to last data point Q_{corr}

$$\Delta H_2^\circ = Q_{corr}/V[M(SO_4)_2^-] + Q_2' \qquad (10)$$

increased from 0 to 8% of Q_{obs} whereas Q_{MSO_4} varied from 95 to 86% of Q_{obs}. Because of the accumulation of errors in Q_{corr} only the last 12 data points ($Q_{corr} > 0{\cdot}04 Q_{obs}$) were considered in calculating ΔH_2°. Initially data were analysed using trial K_2° values in the range 10—100 in steps of 10; data were then analysed using trial values of K_2° in steps of 2 about the apparent region of graphical convergence. The values of K_2° and ΔH_2° obtained graphically had uncertainties of ±5—10% and ±3—8% respectively. However the errors determined by simultaneously varying K_1° by ±10% and ΔH_1° by ±2% were *ca.* 15—37 and 10—90% for K_2° and ΔH_2° respectively. These errors result from the minimal contribution of $Q_{M(SO_4)_2}$ to Q_{obs}. (Only for the two ions Ce^{3+} and Sm^{3+}, which showed exceptional behaviour in calculations for ΔH_1°, was convergence not achieved.)

Results are given in Table 2. The values of K_2° lie in the range 16—55 and are in broad agreement with those reported by Izatt *et al.*[7] (Table 2); the values of ΔH_2° and ΔH_2 ($\sim\Delta H_2^\circ - 1{\cdot}02$ kJ mol^{-1}) are significantly higher than those reported by Izatt *et al.*[7]

(b) *Least-squares analysis.* For the ions Gd^{3+} and Yb^{3+} the results were checked by a general non-linear least-squares analysis for K_2° and ΔH_2° on data points 14—36 inclusive. The general analysis of solution composition was as described above. The least-squares process

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minimised the error square sum $\Sigma\{[SO_4^{2-}]_t(obs) - [SO_4^{2-}]_t(calc)\}_i^2$, in which $[SO_4^{2-}]_t(calc) = [SO_4^{2-}] + [HSO_4^-] + [MSO_4^+] + 2[M(SO_4)_2^-]$. The value of $[M(SO_4)_2^-]$ used in this summation was calculated from equation (11) in which $\Delta H_2°$ is a trial parameter. Convergence was achieved in 7—10 cycles from a range of trial parameters ($K_2°$, $\Delta H_2°$) to give an R factor[30] of

$$[M(SO_4)_2^-] = Q_{corr}/V(\Delta H_2° - Q_2') \qquad (11)$$

0·1—0·3% and an error square sum of 10^{-8}—10^{-7}; there were no systematic trends in the residuals.[31] The results are in close agreement with those obtained by the graphical method (Table 2). However, the very large errors accumulated in some values of $K_2°$ and $\Delta H_2°$ illustrate a limitation of the enthalpimetric method for simultaneously determining these two parameters.

These calculations make apparent some of the problems inherent in studies on ion pairing systems. $\Delta H_1°$ is strongly dependent on the values chosen for $a°$. The use of Spedding–Jaffe activities and $K_1°$ values is justified by the constancy of the calculated $\Delta H_1°$ over a range of concentrations at low $SO_4^{2-} : M^{3+}$ ratios. The ΔH_1 values ($I = 0·10$M, $\Delta H_1 \sim \Delta H_1° - 3$ kJ mol^{-1}) are in reasonable agreement with those derived by Fay and Purdie, $I = 0·30$M. The parameters $K_2°$ and $\Delta H_2°$ could not be determined with precision or accuracy because of the small magnitude of Q_{corr} [equation (10)] with respect to Q_{obs}.

TABLE 2

$K_2°$ and $\Delta H_2°$ for the reactions $MSO_4^+ + SO_4^{2-} \rightleftharpoons M(SO_4)_2^-(aq)$ at 25 °C

	M^{3+}										
	La	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Reported values (ref. 7)											
log $K_2°$	1·85	1·9	1·7	1·8	1·7	1·9	1·75	1·6	1·8	1·8	1·7
$\overline{\Delta H}_2$/kJ mol^{-1} (I = 0·1M)	6·7	4·8	6·7	6·3	6·3	3·2	5·7	6·7	5·7	3·6	4·1
Graphical analysis											
log $K_2°$	1·67 ±0·07	1·30 ±0·05	1·50 ±0·15	1·74 ±0·06	1·55 ±0·07	1·51 ±0·08	1·2 ±0·2	1·3 ±0·2	1·45 ±0·15	1·55 ±0·07	1·6 ±0·2
$\Delta H_2°$/kJ mol^{-1}	17 ± 2	24 ± 3	15 ± 6	9·1 ±1·2	10·9 ±1·3	13 ± 2	21 ± 12	16 ± 14	12 ± 5	8 ± 3	9 ± 3
Least-squares analysis											
log $K_2°$					1·56 ±0·05						1·5 ±0·2
$\Delta H_2°$/kJ mol^{-1}					9·8 ±0·9						9 ± 3

[3/2477 *Received, 4th December*, 1973]

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