A Reinvestigation of the Enthalpy Changes for the Interaction of the Sulphate Ion with some Transition-metal Ions in Aqueous Solution

By **Gavin R. Hedwig** * and **H. Kipton J. Powell**,* Chemistry Department, University of Canterbury, Christchurch, New Zealand

Calorimetric enthalpy data are reported for the interaction of the sulphate ion with divalent Mg, Mn, Co, Cu, and Zn ions in aqueous solution. Data are compared with those from other calorimetric and 'temperature coefficient' studies. The small dependence of $\Delta H°$ on the accuracy of $\log K°$ and the significant dependence of $\Delta H°$ on the choice of mean activity-coefficient expression are discussed. The chosen activity-coefficient expression contributes significantly to the computed solution compositions and to the correction of enthalpy data to infinite dilution; it is mainly these factors which give rise to the variance between reported calorimetric results.

Calorimetrically determined enthalpy changes have recently been reported by Izatt *et al.*[1] for the interaction of the SO_4^{2-} ion with a large number of divalent and trivalent cations in aqueous solution. This work involved a continuous titration calorimetric procedure. A comparison with other enthalpy data determined from the variation of $\log K°$ with T reveals large discrepancies.[2–6] Although enthalpy data calculated from the temperature coefficient of an equilibrium constant are generally regarded as of lower accuracy than those determined by direct calorimetric methods,[7] the large discrepancies are surprising in view of the reasonable agreement which was obtained when the two approaches were applied to the ionisation of bisulphate ion.[8]

Further, Larson[9] has recently reported enthalpy changes for several divalent metal : sulphate interactions; $\Delta H°$ was calculated from heat of dilution data[10] for the 2 : 2 electrolytes. These $\Delta H°$ data concur neither with those of Izatt *et al.*[1] nor with those from temperature coefficient studies.

It was considered desirable to make an independent check on the enthalpy change for a few metal ion–sulphate ion interactions.

The calorimetric enthalpy data are reported for the interaction of SO_4^{2-} ions with hydrated Mg, Mn, Co, Cu, and Zn^{II} ions in aqueous solution, 25 °C, $I = 0$. Data were obtained from titrations of tetramethylammonium sulphate solution into metal chloride solutions, a method analogous to that of Izatt *et al.*[1]

EXPERIMENTAL

Materials and Solutions.—The tetramethylammonium sulphate solution was prepared by adding AnalaR sulphuric acid to a solution of tetramethylammonium hydroxide (B.D.H. *ca.* 25% solution), until the pH was between 6·5 and 7. The sulphate concentration was determined gravimetrically as barium sulphate.[11]

The metal ion chloride solutions, prepared from B.D.H. AnalaR reagents, were standardised by complexometric titrations[12] against EDTA (standardised using AnalaR ZnO).

Procedure.—The incremental titration isoperibol calorimeter and its operation have been described.[13] Increments of $(Me_4N)_2SO_4$ ($0{\cdot}670_0 \pm 0{\cdot}001$M) were added to 98·84 ml of the metal chloride solution (*ca.* 0·02M) in the calorimeter. The resultant endothermic heat changes were corrected for (i) the temperature difference (*ca.* 0·01 °C) between the titrant and the bulk calorimetric solution and (ii) the heat of dilution of the titrant; these corrections were obtained from the dilution of tetramethylammonium sulphate into water and into lithium chloride solution.

RESULTS AND CALCULATIONS

A successive approximations method was used to obtain the solution composition at each titration point. From an approximate value of the ionic strength I, the activity coefficient expression $\gamma_{MSO_4}/\gamma_M\gamma_{SO_4}$ (assuming $\gamma_{MSO_4} = 1$) was calculated and this was used to obtain a value of the concentration quotient K_c from the thermodynamic equilibrium constant $K°$. The solution composition was then calculated, using the mass balance equations for T_M and $T_{SO_4^{2-}}$, and an improved value of I was then obtained. The process was repeated until convergence was obtained. For the reactions with Mg, Mn, and Zn^{II} the solution pH during a titration was between 6 and 7, and no corrections for HSO_4^- formation were necessary. However, for the reactions with Co^{II} and Cu^{II} it was necessary to include a mass balance equation for T_H ($T_H = 4 \times 10^{-5}$ to 8×10^{-5}M), and the iterative procedure was repeated until convergence was achieved for both $[H^+]$ and for $[SO_4^{2-}]$. Convergence was achieved in 3 to 5 cycles; the correction for the formation of HSO_4^- was *ca.* 1% of $\Delta H°$. The calculations were performed using an IBM 360/44 computer. At the concentrations used in this study, the interaction between metal ion and chloride ion is not signifi-

---

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

[2] V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 1958, 3706.

[3] H. W. Jones and C. B. Monk, *Trans. Faraday Soc.*, 1952, **48**, 929.

[4] R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, 1953, **49**, 619.

[5] G. Atkinson and S. K. Kor, *J. Phys. Chem.*, 1967, **71**, 673.

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

[7] E. J. King, 'Acid–Base Equilibria,' International Encyclopedia of Physical Chemistry and Chemical Physics, Pergamon Press, New York, 1965, p. 196.

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

[9] J. W. Larson, *J. Phys. Chem.*, 1970, **74**, 3392.

[10] Ref. 9 and references therein.

[11] A. I. Vogel, 'Textbook of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[12] G. Schwarzenbach and H. Flaschka, 'Complexometric Titrations,' 2nd English edn., Methuen, London, 1969.

[13] G. R. Hedwig and H. K. J. Powell, preceding paper.

TABLE 1

Calorimetric data from the titration of aqueous $ZnCl_2$ solution against $(Me_4N)_2SO_4$ at 25 °C

Volume [a]	Zn [b]	SO_4 [b]	$ZnSO_4$ [b]	Ionic strength/M	K_c [c]	$\log \gamma_{\pm}$ [d]	Q/J [e]	$Q_{corr.}/J$ [f]	$\Delta H/$ kJ mol^{-1} [g]	$-6.8016 \log \gamma_{\pm}/$ kJ mol^{-1} [h]	$\Delta H°/$ kJ mol^{-1}
0·000	1·8700	0·000	0·000	0·0568							
							0·784 (0·801)	0·223	3·957 (4·140)	2·570	6·527 (6·710)
0·500	1·7283	0·1933	0·1417	0·0609	42·1	−0·3778					
							0·709 (0·699)	0·224	4·006 (3·923)	2·642	6·648 (6·565)
1·000	1·6072	0·4071	0·2628	0·0658	40·1	−0·3885					
							0·610 (0·623)	0·226	3·749 (3·876)	2·719	6·468 (6·595)
1·500	1·5049	0·6398	0·3652	0·0714	38·0	−0·3998					
							0·560 (0·576)	0·226	3·884 (4·070)	2·800	6·684 (6·870)
2·000	1·4191	0·8890	0·4512	0·0776	36·0	−0·4116					
							0·504 (0·515)	0·228	3·825 (3·978)	2·880	6·705 (6·858)
2·500	1·3471	1·1521	0·5234	0·0843	34·1	−0·4234					
							0·464 (0·446)	0·229	3·869 (3·573)	2·958	6·827 (6·531)
3·000	1·2866	1·4265	0·5841	0·0914	32·4	−0·4349					

[a] Cumulative volume (ml) of 0·6700M-$(Me_4N)_2SO_4$ titrant added to 98·84 ml of 0·0189$_2$M-$ZnCl_2$. [b] Values are the number of mmoles of each species at each titration point. [c] $\log K° = 2.38$, ref. 2. [d] Calculated using the Davies equation, $-\log \gamma_{\pm} = 0.5085 \times 4\{[\sqrt{I}/(1 + \sqrt{I})] - 0.20I\}$. [e] The measured enthalpy change between successive titration points including a term (*ca.* 4%) for temperature difference between titrant and $ZnCl_2$ solution; data in parentheses were obtained from a second titration under identical conditions. [f] Correction for the heat of dilution of the titrant and for the temperature difference between the titrant and $ZnCl_2$ solution. [g] $\Delta H = (Q - Q_{corr.})/(\text{mmol } ZnSO_4)$. [h] Corrections for the conversion of ΔH to $\Delta H°$.

cant.[14] It was assumed that the formation of $M_2SO_4^{2+}$ and $M(SO_4)_2^{2-}$ is negligible.[15]

TABLE 2

Enthalpy data for M^{2+}–SO_4^{2-} interactions in aqueous solution at 25 °C, $I = 0$

Reaction	$\Delta H°$/kJ mol^{-1}	Method	Ref.
$Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4(aq)$	6·67 ±0·13(12) [a]	Cal.	This work
	2·64 ± 0·08	Cal.	1
	5·56 ± 0·4	Cal.	25
	5·7 ± 0·9	Cal.	9
	16·8 ± 1·7	Temp.	2
$Mn^{2+} + SO_4^{2-} \rightleftharpoons MnSO_4(aq)$	9·09 ± 0·19(5)	Cal.	This work
	2·55 ± 0·04	Cal	1
	14·1 ± 1·3	Temp.	6
$Mg^{2+} + SO_4^{2-} \rightleftharpoons MgSO_4(aq)$	6·50 ± 0·17(6)	Cal.	This work
	2·13 ± 0·13	Cal.	1
	5·48 ± 0·4	Cal.	25
	5·3 ± 0·8	Cal.	9
	20·2 ± 1·7	Temp.	2
$Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4(aq)$	10·18 ± 0·25(5)	Cal.	This work
	5·10 ± 0·1$_3$	Cal.	1
	8·08 ± 0·4	Cal.	25
	7·2 ± 0·8	Cal.	9
$Co^{2+} + SO_4^{2-} \rightleftharpoons CoSO_4(aq)$	6·17 ± 0·09(4)	Cal.	This work
	2·09 ± 0·08	Cal.	1
	5·48 ± 0·4	Cal.	25
	7·28 ± 0·67	Temp.	6

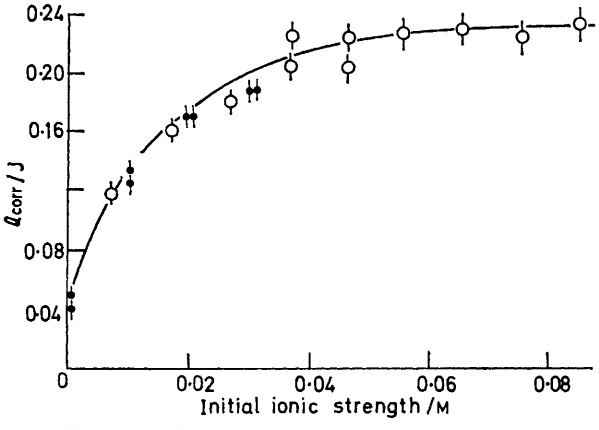
[a] The mean ± the standard deviation from the mean; number of data in parentheses.

The results from a titration of $(Me_4N)_2SO_4$ against $ZnCl_2$ are shown in Table 1. The heat changes Q were reproducible to ±2 to 4%.

The enthalpy data for the interaction of sulphate ions with the metal ions are shown in Table 2. For comparison, data determined by other workers are also tabulated.

DISCUSSION

Heat of Dilution of Tetramethylammonium Sulphate.—Izatt and his co-workers[1] reported the heat of dilution of a 0·7006M-solution as a power series in $I^{\frac{1}{2}}$. The dilution data in this study (0·670M-titrant) could not be interpreted in terms of their power series.



(○), Titration of 0·6700M-$(Me_4N)_2SO_4$ into LiCl solution; (●), titration of 0·6700M-$(Me_4N)_2SO_4$ into HO_2

Studies of the heat of dilution of $LiClO_4$ solution into Li_2SO_4 solution and into $LiClO_4$ solution[16] indicated that the heat change for the interaction of Li^+ and SO_4^{2-} is zero. In this study the heat of dilution of the titrant into water and into LiCl solution was endothermic. All the data lay on a smooth curve of Q against the solution (initial) ionic strength (Figure) irrespective

---

[14] L. G. Sillen and A. E. Martell, 'Stability Constants,' *Chem. Soc. Special Publ.*, No. 17, 1964 and No. 25, 1971.

[15] K. S. Pitzer, *J.C.S. Faraday II*, 1972, 101.

[16] J. M. Austin and A. D. Mair, *J. Phys. Chem.*, 1962, **66**, 519.

of the [Cl^-]. [Approximately 10% of the observed heat change for dilution arises from the temperature difference (*ca.* 0·01°) between titrant and calorimeter solution.[13] This latter term was eliminated when the observed heat of reaction was corrected for the heat change for titrant dilution.] This result suggests that the interaction of the Me_4N^+ ion and Cl^- ion is zero. Evans and Kay[17] reported that the interaction between Me_4N^+ and Cl^- is not significant, although reinterpretation of their data[18] gave an association constant $K = 1{\cdot}09$ for the interaction.

Metal–Sulphate Interactions.—The data in Table 1 reveal that in the calculation of ΔH° two large corrections must be applied to the measured heat change. These corrections are (i) for dilution of the titrant, and (ii) for conversion of ΔH to ΔH°. The importance of the former term, Q_{corr}, is obvious from its magnitude compared with the measured heat change Q. The latter correction is given by $\Delta H^\circ - \Delta H = -2RT^2[\partial (\ln \gamma_\pm)/\partial T]_P$[19] $= -4 \times 10^{-3} RT^2 \ln \gamma_\pm$[20] $= -6{\cdot}80 \log \gamma_\pm$ for the reaction $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$ (aq.). The magnitude of this correction is dependent on the expression used to calculate the mean ionic activity coefficient $\gamma_\pm$ for the electrolyte $M^{2+}SO_4^{2-}$. In this work the empirical Davies' equation[21] was used to calculate $\log \gamma_\pm$.

The ΔH° data for $Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4(aq)$ in Table 3 illustrate the effect of (i) choice of different log K° values and (ii) choice of different activity coefficient expressions. Nair and Nancollas[2] reported an average association constant of $10^{2{\cdot}38}$ with an uncertainty range from $10^{2{\cdot}35}$ to $10^{2{\cdot}40}$. On changing the value of log K° from 2·38 to 2·35 the average ΔH° increased by 0·17 kJ mol⁻¹. This change arises mainly from a change in the (calculated) number of mmol of $ZnSO_4$(aq) present at each titration increment; there was only a very small change in the ionic strength and in the activity coefficient term (*e.g.* for the last data point in Table 1, using log $K^\circ = 2{\cdot}35$; $[ZnSO_4] = 0{\cdot}56058$, $I = 0{\cdot}0923$, $K_c = 30{\cdot}0$, $\log \gamma_\pm = -0{\cdot}4364$).

The results in Table 3 show that the use of different activity coefficient expressions (see footnote to Table 3) leads to widely different average ΔH° values. The difference arises both from the change in the (computed) solution composition due to different K_c values (for example using Izatt's mean ionic activity coefficient expression and log $K^\circ = 2{\cdot}38$, the K_c values range from 61·1 to 55·5 for the data points in Table 1), and from the correction to infinite dilution. The approach by Izatt *et al.*[8] in choosing an activity coefficient expression was to allow C in the equation to vary, the 'correct' value of

$$-\log \gamma_\pm = Z^2A[I^{\frac{1}{2}}/(1 + Ba^\circ I^{\frac{1}{2}})] - CZ^2I$$

C being that which gave the minimum value of the error square sum in their calculation procedure.[8] However their value of $CZ^2 = 1{\cdot}0 \pm 0{\cdot}2$ is not in good agreement with the parameters in the closely related Davies' equation (which does predict the mean ionic activity coefficients of a large number of simple electrolytes up to 0·1M[21]) and leads to abnormally high activity coefficients.[22]

The enthalpy data from this work (Table 2) were calculated using the log K° values determined by Nair and Nancollas[2] and (for copper) by Bale, Davies, and Monk[23] and using the Davies' equation for log $\gamma_\pm$. The data are significantly different from those reported from the temperature coefficient of log K°.[2,3,5,6] Our ΔH° data do not agree with those of Izatt *et al.*[1] (which were determined using concentration conditions similar to those in this study); the discrepancy arises from use of a different value for $K_c = K^\circ(\gamma_\pm)^2$ and because their enthalpy data, although quoted as ΔH°, were not corrected to infinite dilution.[24] However when our data for Zn^{II} are calculated using the log K° value and the activity coefficient expression reported by Izatt *et al.*, the average ΔH value obtained from this work for the Zn^{2+}–SO_4^{2-} interaction is 2·65 ± 0·18 kJ mol⁻¹ (I = 0·06—0·08M), which compares favourably with the value obtained by Izatt *et al.* (2·64 ± 0·08 kJ mol⁻¹).

TABLE 3

Enthalpy data for $Zn^{2+} + SO_4^{2-} \rightleftharpoons ZnSO_4(aq)$ obtained using various equilibrium constants and activity coefficient expressions[a]

log K°	Activity coefficient expression	ΔH°/kJ mol⁻¹ [b]
2·49	A = 0·5115, B = 0·3291 a° = 5Å, C = 0·25 [c]	4·73 ± 0·14 [e]
2·38	As above	5·04 ± 0·20
2·38	A = 0·5085 [d]	6·64 ± 0·13
2·35	A = 0·5085 [d]	6·81 ± 0·17
2·35	A = 0·5115 [d]	6·86 ± 0·13

[a] Calculations performed using the six data points in Table 1. [b] Values are the means and standard deviations. [c] $\log \gamma_\pm = -AZ^2[\sqrt{I}/(1 + Ba^\circ\sqrt{I})] + CZ^2I$, ref. 1. [d] $\log \gamma_\pm = -AZ^2[\sqrt{I}/(1 + \sqrt{I})] + 0{\cdot}20I$, ref. 21. [e] When the data are not corrected to $I = 0$, the mean ΔH = 2·65 ± 0·18 kJ mol⁻¹.

Calorimetric enthalpy data have been determined by Austin and Mair,[25] from the difference between the heat of dilution of Li_2SO_4 into $LiClO_4$ solution and into $M(ClO_4)_2$ solution, at a final ionic strength of 0·035M. The enthalpy changes corrected to infinite dilution are in satisfactory agreement with those determined in this study (Table 2). In their work, the solution composition was calculated using the association constants reported by Nancollas,[2] and activity coefficients were calculated using the Davies' equation.[21] From the heats of dilution of metal sulphate solutions Larson[9] has calculated the

---

[17] D. F. Evans and R. L. Kay, *J. Phys. Chem.*, 1966, **70**, 366.

[18] R. Fernandez-Prini, *Trans. Faraday Soc.*, 1968, **64**, 2146.

[19] H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*B*), 1966, 1205.

[20] H. J. V. Tyrrell and G. L. Hollis, *Trans. Faraday Soc.*, 1952, **48**, 893.

[21] C. W. Davies, 'Ion Association,' Butterworths, London, 1962, p. 39.

[22] S. Cabani and P. Gianni, *Analyt. Chem.*, 1972, **44**, 253.

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

[24] R. M. Izatt, communication to H. K. J. Powell.

[25] J. M. Austin and A. D. Mair, unpublished work.

enthalpy change for formation of metal ion–sulphate ion pairs; the resultant ΔH° values are in satisfactory agreement with those of Austin and Mair and with those quoted for this study. Although Larson's approach has the limitation of using only one metal to sulphate ratio it has the advantage of minimising corrections of enthalpy data to infinite dilution. His results carry a significant experimental uncertainty.

We acknowledge correspondence on this subject with Professor G. H. Nancollas.

[2/2324 *Received*, 10*th October*, 1972]