Entropy Titrations: A Reassessment of Data for the Reaction of the Sulphate Ion with Protons and with Bivalent Metal Ions

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The method of simultaneous determination of log K° and ΔH° for anion–cation interactions is critically discussed by reference to the reactions $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ and $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$. For these reactions the ' entropy titration ' approach is less reliable than that employing potentiometrically determined K° data to calculate ΔH° from calorimetric measurements. The effects of the choice of activity coefficient expression are discussed. A general non-linear least-squares procedure has been used for the simultaneous determination of ΔH° and K°. The procedure is contrasted with the iterative method used by other workers. ΔH° for $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$ have been recalculated by use of potentiometric K° data and published calorimetric data.

Recently the method of simultaneous determination of ΔH° and K° from enthalpimetric titrations has been developed.[1] Results have been published for the reactions $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$,[1,2] $M^{n+} + SO_4^{2-} \rightleftharpoons MSO_4^{(n-2)+}$,[3] and many others.[4-8] It has been shown[1] that for a reaction $A + B \rightleftharpoons AB$ an expression

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

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

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

[4] J. J. Christensen, R. M. Izatt, and D. Eatough, *Inorg. Chem.*, 1965, **4**, 1278.

[5] J. J. Christensen, D. P. Wrathall, R. M. Izatt, and D. O. Tolman, *J. Phys. Chem.*, 1967, **71**, 3001.

[6] R. M. Izatt, D. Eatough, and J. J. Christensen, *J. Phys. Chem.*, 1968, **72**, 2720.

[7] P. Paoletti, A. Vacca, and D. Arenare, *J. Phys. Chem.*, 1966, **70**, 193.

[8] R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore, and J. J. Christensen, *Science*, 1969, **164**, 443.

of the form (1) can be written, where D, E, and F are expressions relating total concentrations of A and B,

$$\frac{\Delta H}{K} = D(\Delta H)^2 + E\Delta H + F \qquad (1)$$

volume, the measured heat change, and the product of activity coefficients for A, B, and AB. From a set of equations (1) for a given reaction ΔH and K can be determined by solution of simultaneous equations [1] such as (2) or by iterative [7,9-11] or general non-linear least-squares procedures.

$$(D_2 - D_1)\Delta H^2 + (E_2 - E_1)\Delta H + (F_2 - F_1) = 0 \quad (2)$$

Different workers have pointed to the limitations [9,10,12] and to the advantages [1,10] of this method which was first reported by Becker *et al.*[13] and advanced by Christensen, Izatt, and their co-workers. This paper (i) discusses certain limitations and disadvantages of this method, (ii) discusses the dependence of the results on the relationships used for the minimisation of residuals, and (iii) refers to the profound effect of the chosen activity coefficient expression on the computed ΔH° and K° for ion-pairing reactions.

Dissociation of the Hydrogensulphate (*Bisulphate*) *Ion*.—Cabani and Gianni [9] have critically examined the simultaneous calculation of ΔH and $\log K^\circ$ for the reaction (3).

$$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+ \qquad (3)$$

They drew attention to the dependence of K° and ΔH on the choice of activity coefficient expression and on the corrections made to Q_{obs} for the side reactions occurring in the calorimeter, *e.g.*, dilution of titrant ($HClO_4$) or formation of ion pairs ($NaSO_4^-$). However, in their calculations Cabani and Gianni [9] and Izatt *et al.*[1,2] have not allowed for the dependence of ΔH on the ionic strength; they have therefore derived an average value of the concentration-dependent molar enthalpy change, $\overline{\Delta H}$. Further, these workers [1,2,9-11] and others [7] have used only iterative procedures to calculate the 'best' values of ΔH and K°. This procedure is less reliable and less rigorous than a general non-linear least-squares process which, by independently varying *all* parameters, seeks a minimum in the error square sum $U = \Sigma(F_{obs} - F_{calc})^2$ where F is an analytical or experimentally observed quantity; the process terminates when for all parameters $\partial(U)/\partial$ (parameter) $= 0$. The iterative procedure [7,10,11] varies only one parameter (usually K) and for each value of K calculates the solution composition for each data point, an average value of the enthalpy change (4), and an error square sum (5) [or an equivalent expression (6) where $\Delta H_i = (q_r/M_{AB})_i$]. The 'best pair,' K°, $\overline{\Delta H}$,

$$\overline{\Delta H}_{AB} = \frac{1}{n}\sum_{i=1}^{n}\left(\frac{q_r}{M_{AB}}\right)_i \qquad (4)$$

$$U = \sum_{i=1}^{n}\{w_i(\overline{\Delta H}_{AB} - \Delta H_i)^2\} \qquad (5)$$

$$U = \sum_{i=1}^{n}\{w_i(q_i - \overline{\Delta H}_{AB}M_{AB})^2\} \qquad (6)$$

corresponds to the minimum in the function U. However the quantity $\overline{\Delta H}$ is a function of K° and therefore $U = f(K, [A]_t, [B]_t)$, whereas, as pointed out by Sillen,[14] the expression used for F must be complete and contain all terms which should be independently varied, *i.e.*, it is required that $U = f(K^\circ, \Delta H^\circ, [A]_t, [B]_t)$ and that U be minimised for both K° and ΔH°. Further, the minimum value of U results for the value of K° which gives the smallest spread of ΔH_i values such that $\overline{\Delta H} - \Delta H_i$ is a minimum through the data set. If there are any systematic uncertainties associated with q_r, $[A]_t$, or $[B]_t$ then the correct (rather than 'best') value of K° will give a set of ΔH_i which show a drift; the iterative process will choose an incorrect K° to minimise this drift. Also if (as assumed by the above workers [1,2,9]) ΔH_i is the concentration-dependent enthalpy change, then for the correct value of K° the ΔH_i values *must* span a significant range (*ca.* 0·7 kJ mol^{-1} for $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$; Table 1). Thus minimisation of the sum of squared residuals $(\overline{\Delta H}_{AB} - \Delta H_i)^2$ must yield an incorrect value for K°.

In reassessing the data for HSO_4^- proton dissociation Cabani and Gianni have used only those activity coefficient expressions employed by Izatt *et al.*[1,2], *viz.*, (7) and (8), although the latter expression leads to

$$\log \gamma_\pm = \frac{-Az^2\sqrt{I}}{1 + 1{\cdot}65\sqrt{I}} \qquad (7)$$

$$\log \gamma_\pm = -Az^2\left\{\frac{\sqrt{I}}{1 + 1{\cdot}65\sqrt{I}} - 0{\cdot}5I\right\} \qquad (8)$$

abnormally high activity coefficients.[9] Two other empirical equations which have been proven applicable to hydrogensulphate or sulphate ion systems are the two forms of the Davies equation (9) where $\beta = 0{\cdot}2$ [15-20]

$$\log \gamma_\pm = -Az^2\left\{\frac{\sqrt{I}}{1 + \sqrt{I}} - \beta I\right\} \qquad (9)$$

or 0·3.[21,22] Using each Davies equation and equation

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

[10] J. J. Christensen, D. P. Wrathall, J. O. Oscarson, and R. M. Izatt, *Analyt. Chem.*, 1968, **40**, 1713.

[11] R. M. Izatt, D. Eatough, R. Snow, and J. J. Christensen, *J. Phys. Chem.*, 1968, **72**, 1208.

[12] S. Cabani and P. Gianni, *J. Chem. Soc.* (*A*), 1968, 547.

[13] F. Becker, J. Bartel, N. G. Schmahl, G. Lange, and H. M. Luschow, *Z. phys. Chem.* (*Frankfurt*), 1963, **37**, 33.

[14] L. G. Sillen, *Acta Chem. Scand.*, 1962, **16**, 159.

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[17] V. S. K. Nair and G. H. Nancollas, *J. Chem. Soc.*, 1959, 3936.

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[19] C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

[20] C. W. Davies, H. W. Jones, and C. B. Monk, *Trans. Faraday Soc.*, 1952, **48**, 921.

[21] C. W. Davies, 'Ion Association,' Butterworths, London, 1962, p. 44.

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

(8) to calculate activity coefficients we have recalculated ΔH° and K° for the dissociation of the hydrogensulphate ion from the data of Izatt *et al.*[23] (Table 1). The data used were for the titrations of 0·7006M-$(Me_4N)_2SO_4$ into 0·01665M-$HClO_4$ (ref. 23, run 12, 35 data points); Q_{obs} was corrected for the heat of dilution of the titrant[3] for the formation of the ion pair $Me_4N^+ClO_4^-$ ($\log K = 0{\cdot}27$, $\overline{\Delta H} = 0{\cdot}84$ kJ mol^{-1}).[2] Molar concentrations were used because of the small temperature changes involved in the calorimetric measurements (max. 0·05 °C). The calculations used the previously described[24] general non-linear least-squares programme to determine the best value for the constants ΔH° and K°.

TABLE 1

Simultaneous solutions of ΔH° and K° from enthalpimetric titrations for the reaction $SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-(aq)$ at 25 °C [a]

Method	ΔH° / kJ mol^{-1}	K°	$\log K^\circ$	$\Sigma(F_{obs} - F_{calc})^2$	R [b] (%)
$\log \gamma_\pm = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+\sqrt{I}} - 0{\cdot}2I\right\}$ [c]	26·4 ± 0·5	99·5 ± 4·2	1·998 ± 0·018	$1{\cdot}20 \times 10^{-6}$	0·29
$\log \gamma_\pm = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+\sqrt{I}} - 0{\cdot}3I\right\}$ [d]	23·3 ± 0·4	109·4 ± 4·2	2·039 ± 0·018	$1{\cdot}18 \times 10^{-6}$	0·29
$\log \gamma_\pm = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+1{\cdot}65\sqrt{I}} - 0{\cdot}5I\right\}$ [e]	19·6 ± 0·2	142·4 ± 3·6	2·153 ± 0·011	$0{\cdot}81 \times 10^{-6}$	0·24
$\log \gamma_\pm = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+1{\cdot}65\sqrt{I}} - 0{\cdot}5I\right\}$ [f] assuming $\Delta H = \Delta H^0$	17·8 ± 0·6	161·6 ± 14·7	2·208 ± 0·038	$1{\cdot}65 \times 10^{-5}$	1·09
Reported by Izatt *et al.*	20·5 ± 0·8	93·3 ± 6·7	1·97 ± 0·03		
Calc. $\overline{\Delta H}$ by imposing Izatt's $\log K^\circ$ and and $\log \gamma_\pm$ values on least-squares refinement	21·74 ± 0·08	93·3	1·97	$2{\cdot}28 \times 10^{-5}$	1·26

[a] Data from ref. 23; 35 data points for the titration of $(Me_4N)_2SO_4$ into $HClO_4$. Corrections applied for titrant dilution (ref. 3) and $R_4N^+ClO_4^-$ ion pairing (ref. 2). [b] R defined as in equation (19) (ref. 29). [c] Computed ionic strength range 0·0176—0·101M, ΔH range 24·2—23·6 kJ mol^{-1}; q_{diln} in range 0·0054—0·874 J and q(ion pair) in range 0·00808—2·281 J for individual data points which range from 1·021 to 21·43 J. [d] Computed ionic strength range 0·0175—0·098M; ΔH range 22·6—22·1 kJ mol^{-1}. [e] Computed ionic strength range 0·0172—0·0915M; ΔH range 18·9—18·4 kJ mol^{-1}. [f] Computed ionic strength range 0·0171—0·0900M.

For the reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ we obtain equation (11) where $[HSO_4]$ is given by (12) and ΔH by (13)[25] and (14) for the protonation of sulphate ion.

$$K_c = K^\circ \frac{\gamma_{H^+}\gamma_{SO_4^{2-}}}{\gamma_{HSO_4^-}} = K^\circ \gamma_{SO_4^{2-}} = K^\circ \gamma_\pm \tag{10}$$

$$= \frac{[HSO_4]}{([H]_t - [HSO_4])([SO_4]_t - [HSO_4])} \tag{11}$$

$$[HSO_4] = \frac{Q_{corr}(J)}{V(ml) \cdot \Delta H(kJ\ mol^{-1})} \tag{12}$$

$$\Delta H = \Delta H^\circ - RT^2\Sigma\left[n_s \frac{\partial \ln f_s}{\partial T}\right]_p \tag{13}$$

$$= \Delta H^\circ + 2{\cdot}303RT^2\left[\frac{\partial \log \gamma_{SO_4^{2-}}}{\partial T}\right]_p \tag{14}$$

For the activity coefficient expressions employed, (15), we obtain equation (16), if C is taken as constant.

$$-\log \gamma_\pm = Az^2\left\{\frac{\sqrt{I}}{1+B\sqrt{I}} - CI\right\} \tag{15}$$

$$-\frac{\partial \log \gamma}{\partial T} = Az^2 \frac{\sqrt{I}}{1+B\sqrt{I}}\left\{\frac{1}{A}\frac{dA}{dT} + \frac{1}{1+B\sqrt{I}}\frac{1}{2I}\frac{dI}{dT} - \frac{B\sqrt{I}}{1+B\sqrt{I}}\frac{1}{B}\frac{dB}{dT}\right\} - z^2ACI\left\{\frac{1}{A}\frac{dA}{dT} + \frac{1}{I}\frac{dI}{dT}\right\} \tag{16}$$

From the expressions for A $[=k(\varepsilon T)^{-3/2}]$[26] and B $[=k'(\varepsilon T)^{-1/2}]$[26] and from the relationship $d\varepsilon/dT = -4{\cdot}5 \times 10^{-3}\varepsilon_{H_2O}$ (25 °C)[27] the terms $(1/A)(dA/dT)$ and $(1/B)(dB/dT)$ are calculated as $1{\cdot}85 \times 10^{-3}$ and $0{\cdot}62 \times 10^{-3}$ respectively at 25 °C. If the solution is assumed to have the same thermal coefficient of expansion as the solvent then we obtain equation (17) at 25 °C, where V_m is the molar volume of water.[28]

If equation (16) is written as a function of I, $C'(I)$, rearrangement of equation (11) gives equation (18).

$$\frac{1}{I}\frac{dI}{dT} = -\frac{1}{V_m}\frac{dV_m}{dT} = -2{\cdot}58 \times 10^{-4} \tag{17}$$

$$[SO_4]_t = \frac{\dfrac{Q_{corr}}{K^\circ\gamma_\pm} + Q_{corr}[H^+]_t - \dfrac{(Q_{corr})^2}{[\Delta H^\circ + 2{\cdot}303RT^2C'(I)]V}}{[H]_tV[\Delta H^\circ + 2{\cdot}303RT^2C'(I)] - Q_{corr}} \tag{18}$$

The least-squares process varied both the parameters ΔH° and K° to minimise the error square sum $\Sigma w_i\{[SO_4]_t(obs) - [SO_4]_t(calc)\}_i^2$. Following the first least-

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[23] Data supplementary to ref. 2; document No. 00184 obtained from ASIS National Auxiliary Publication Serivce, c/o CCM Information Services, 22 West 34th Street, New York, 10001.

[24] G. R. Hedwig and H. K. J. Powell, *Analyt. Chem.*, 1971, **43**, 1206.

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

[26] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959, 2nd edn., p. 230.

[27] R. L. Kay, G. A. Vidulich, and K. S. Pribadi, *J. Phys. Chem.*, 1969, **73**, 445.

[28] Ref. 26, p. 457.

squares cycle, which used trial values of K°, ΔH°, and I, each cycle commenced by using the improved K° to calculate the solution composition, and hence to calculate an improved value of I and of $\gamma_\pm$ for use in equation (18). The least-squares process terminated when the error square sums for successive cycles of refinement differed by less than 0·1%. A weighting factor $w_i = 1{\cdot}0$ was used.

The results in Table 1 indicate the strong dependence of both ΔH° and K° on the equation used for log $\gamma_\pm$. The titration data span the ionic strength range *ca.* 0·017—0·10, and although equations (8) and (9) give similar values for $\gamma_\pm$ at $I = 0{\cdot}02$ {*viz.*, 0·569 [equation (9), $\beta = 0{\cdot}2$]; 0·574 [equation (9), $\beta = 0{\cdot}3$]; 0·612 [equation (8)]}, the calculated coefficients differ markedly at $I = 0{\cdot}09$ (0·369, 0·384, and 0·481 respectively). For comparison, Table 1 records results obtained by use of Izatt's equation and the assumption[1] that $\Delta H^\circ = \overline{\Delta H}$. Footnotes record the computed ionic strength range and the range of values for ΔH for each calculation. The programme gave convergence in 4 or 5 cycles (3 min on an IBM 360/44 computer) except for the calculation which assumed that $\Delta H^\circ = \overline{\Delta H}$; in the latter case, after 10 cycles, the parameters were ranging in the area $K^\circ = 160$—170 l mol^{-1} and $\Delta H^\circ = 17{\cdot}4$—17·9

$$R = \sqrt{\left(\frac{\Sigma(F_{\text{obs}} - F_{\text{calc}})^2}{\Sigma(F_{\text{obs}})^2}\right)} \cdot \frac{100}{1}\% \qquad (19)$$

kJ mol^{-1}. Each calculation achieved an R factor[26] of *ca.* 0·3%.

It is appreciated[29,30] that a good fit between calculated and experimental data is often insufficient support for hypotheses on an equilibrium system. For protonation of the sulphate ion at least three approaches yield a good fit (Table 1). One has to decide which combination of ΔH° and K° (which result from different activity coefficient expressions) most closely approaches the ' correct ' result; this is a problem which does not arise when an independently determined K° value is used in the calculation of ΔH°.

The results in Table 1 can be compared with the ' best ' values of log K° (potentiometric) and ΔH°, *viz.*, log $K^\circ = 1{\cdot}988$[9,31] and $\Delta H^\circ = 24{\cdot}0$ kJ mol^{-1} (Austin and Mair;[32] $HClO_4$ dilution into H_2SO_4, $I = 0{\cdot}02$, corrected to $I = 0{\cdot}0$) and 22·6 kJ mol^{-1} (Readnour and Cobble,[33] data recalculated by Cabani and Gianni;[9] Na_2SO_4 solution in HCl, $I = 0{\cdot}01$—0·03, extrapolated to $I = 0{\cdot}0$). This comparison suggests that results obtained by use of the Davies equation ($\beta = 0{\cdot}2$ or 0·3) for the activity coefficient are the most acceptable. The lack of agreement between the results in Table 1 and Izatt's results relates to the different methods used in the minimisation process. Imposition of the value log $K^\circ = 1{\cdot}97$ on the least-squares programme does yield $\overline{\Delta H} = 21{\cdot}74 \pm 0{\cdot}09$ in concurrence with Izatt's result but the error square sum is significantly higher for this ' solution ' (Table 1).

The agreement between, on the one hand, calorimetric ΔH° and potentiometric K° values, and on the other ΔH° and K° values derived simultaneously from enthalpimetric titrations on this reaction, has been used to establish the reliability of the entropy titration method.[1] However, on the basis of the above arguments and of extensive studies on bivalent cation–sulphate ion interactions (next section) we believe that the agreement achieved in the case of the hydrogensulphate proton dissociation reaction is fortuitous and does not justify confidence in the method.

Formation of Metal(II)*-Sulphate Ion Pairs.*—The dependence of the computed ΔH° and K° on the activity coefficient expression will now be more marked because (i) the relationships $K_c = K^\circ\gamma_\pm$ and $\Delta H = \Delta H^\circ + 2{\cdot}303RT^2C'(I)$, valid for sulphate protonation, are replaced by $K_c = K^\circ(\gamma_\pm)^2$ and $\Delta H = \Delta H^\circ + 2[2{\cdot}303RT^2C'(I)]$ respectively, and (ii) for the reactions $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$ the enthalpy titrations reported[3,34] involve a higher and wider range of ionic strengths (*ca.* 0·06—0·14M) than for the reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$.[2,23]

The ΔH° and K° data in Table 2 have been computed from published enthalpimetric titration data[34] by use of the Davies equation and equation (8) to calculate activity coefficients. The titration data refer to the addition of $(Me_4N)_2SO_4$ (0·7006M) into a metal perchlorate solution (*ca.* 0·02M, pH *ca.* 3—5). The nonlinear least-squares programme minimised the error square sum $\Sigma\{[SO_4]_t(\text{obs}) - [SO_4]_t(\text{calc})\}_i^2$ where $[SO_4]_t$(calc.) is given by equation (20). Following the first

$$[SO_4]_t(\text{calc}) = \frac{\left[\dfrac{Q_{\text{corr}}}{K^\circ(\gamma_\pm)^2} + Q_{\text{corr}}[M]_t - \dfrac{(Q_{\text{corr}})^2}{\{\Delta H^\circ + 2[2{\cdot}303RT^2C'(I)]\}V}\right]}{[M]_tV\{\Delta H^\circ + 2[2{\cdot}303RT^2C'(I)]\} - Q_{\text{corr}}} \qquad (20)$$

cycle, which used trial values of K°, ΔH°, and I, and calculated an approximate correction for titrant dilution, successive cycles commenced by using the improved K° to calculate the solution composition and thus calculate improved values of I and $\gamma_\pm$; Q_{obs} was corrected for the formation of the ion pair $Me_4N^+ClO_4^-$ and for the protonation of the sulphate ion.

The results are critically dependent on the activity coefficient expression used. Convergence was not achieved for each combination of reaction and activity coefficient expression. For each combination one of the two following results was obtained: (i) the least-squares values of K° and ΔH° were quite unrelated to those determined by direct methods, *e.g.*, for zinc, with

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[29] A. Vacca, A. Sabatini, and M. A. Gristina, *Co-ordination Chem. Rev.*, 1972, **8**, 45.

[30] A. M. Bond, *Co-ordination Chem. Rev.*, 1971, **6**, 377.

[31] G. H. Nancollas, ' Interactions in Electrolyte Solutions,' Elsevier, New York, 1966.

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

[33] J. M. Readnour and J. W. Cobble, *Inorg. Chem.*, 1969, **8**, 2174.

[34] Data supplementary to ref. 3; document No. 00185 obtained from ASIS National Auxiliary Publication Service, c/o CCM Information Services, 22 West 34th Street, New York, 10001.

$\log \gamma_{\pm} = -2{\cdot}034\{[\sqrt{I}/(1+\sqrt{I})] - 0{\cdot}3I\}$; in these cases it was further established that the solution obtained did correspond to a minimum value of the error square sum (see below); (ii) the programme could not determine a minimum value for the error square sum: either $K°$ and $\Delta H°$ fluctuated within a broad range (*e.g.* for magnesium, with $\log \gamma_{\pm} = -2{\cdot}034\{[\sqrt{I}/(1+\sqrt{I})] - 0{\cdot}3I\}$ or one of the parameters was divergent.

TABLE 2

Least-squares $K°$ and $\Delta H°$ values from enthalpimetric titrations [a] for reactions $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4(aq)$

Method [b]	$\dfrac{\Delta H°}{\text{kJ mol}^{-1}}$	$K°$	$\log K°$	$\Sigma(F_{obs} - F_{calc})^2$
	Zinc sulphate			
Davies equation, $\beta = 0{\cdot}2$	NC [c]	NC		
Davies equation, $\beta = 0{\cdot}3$	$9{\cdot}5 \pm 0{\cdot}4$	$95{\cdot}0 \pm 8{\cdot}1$	1·98	$2{\cdot}1 \times 10^{-6}$
Equation (8)	NC	NC		
Davies equation, $\beta = 0{\cdot}2$, $K° = 240$ [d] imposed	$6{\cdot}72 \pm 0{\cdot}03$		2·38	$4{\cdot}5 \times 10^{-5}$
Davies equation, $\beta = 0{\cdot}3$, $K° = 240$ [d] imposed	$6{\cdot}44 \pm 0{\cdot}02$		2·38	$3{\cdot}2 \times 10^{-5}$
Equation (8), $K° = 309$ [e] imposed, $\Delta H° = \Delta H$	$2{\cdot}68 \pm 0{\cdot}01$		2·49	$2{\cdot}3 \times 10^{-4}$
Equation (8), reported values [e]	$2{\cdot}64 \pm 0{\cdot}08$		$2{\cdot}49 \pm 0{\cdot}04$	
	Magnesium sulphate			
Davies equation, $\beta = 0{\cdot}2$	4·4—5·2	230—310		
Davies equation, $\beta = 0{\cdot}3$	$4{\cdot}6$—$4{\cdot}8 \pm 0{\cdot}5$	265—324		
Equation (8)	NC	NC		
Equation (8), $K = 169$ [e] imposed, $\Delta H° = \Delta H$	$2{\cdot}11 \pm 0{\cdot}05$		2·23	$4{\cdot}1 \times 10^{-4}$
Equation (8), reported values [e]	$2{\cdot}24 \pm 0{\cdot}12$		2·23	
	Cobalt sulphate			
Davies equation, $\beta = 0{\cdot}2$	$11{\cdot}4 \pm 0{\cdot}8$	$71{\cdot}0 \pm 9{\cdot}0$	1·85	$2{\cdot}2 \times 10^{-6}$
Davies equation, $\beta = 0{\cdot}3$	$8{\cdot}15 \pm 0{\cdot}32$	116 ± 10	2·066	$2{\cdot}8 \times 10^{-6}$
Equation (8) $\Delta H° = \Delta H$	NC	NC		
Davies equation, $\beta = 0{\cdot}2$, $K = 224$ [f] imposed	$6{\cdot}53 \pm 0{\cdot}02$		2·35	$2{\cdot}8 \times 10^{-5}$
Equation (8), $K = 490$ [e] imposed, $\Delta H° = \Delta H$	$2{\cdot}19 \pm 0{\cdot}01$		2·69	$1{\cdot}4 \times 10^{-5}$
Equation (8), reported value [e]	$2{\cdot}09 \pm 0{\cdot}08$		$2{\cdot}69 \pm 0{\cdot}03$	

[a] Data from ref. 34 for reactions described in ref. 3. [b] The expression used to calculate activity coefficients; where a $K°$ value was imposed, only $\Delta H°$ varied in the least-squares process. [c] No convergence achieved. [d] Ref. 16. [e] Ref. 3. [f] Ref. 17.

The effect of ignoring the ion pairing reaction between Me_4N^+ and ClO_4^- was to increase $\Delta H°$ by 40—65%; the profound effect of this side reaction between countercation and anion can be avoided by use of metal chloride solutions.[35] Further insight into the uncertainties associated with previously described calculation methods [9-11] was achieved by imposing a fixed value of $K°$ on the programme and then determining the least-squares value of $\Delta H°$ (Table 2). Use of $K°$ values published by Izatt *et al.*[3] gave $\overline{\Delta H}$ values in agreement with those reported by these workers. Use of $K°$ values reported by Nair and Nancollas [16,17] from potentiometric measurements gave $\Delta H°$ values in fair agreement with those obtained by direct calorimetric measurements.[35] However, in each case the use of these fixed values for $K°$ gave a least-squares solution with a larger error square sum than that for the solution achieved by allowing both parameters to vary.

TABLE 3

Enthalpy data [a] for reactions $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4(aq)$ at 25 °C

	M^{2+}							
	Mg	Ca	Mn	Co	Ni	Cu	Zn	Cd
$\log K°$	2·25 [b]	2·31 [c]	2·26 [d]	2·35 [d]	2·32 [d]	2·33 [e]	2·38 [b]	2·29 [f]
$\Delta H°$/kJ mol^{-1} $\left(\text{assuming } \log \gamma_{\pm} = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+\sqrt{I}} - 0{\cdot}2I\right\}\right)$	$5{\cdot}74 \pm 0{\cdot}13$	$7{\cdot}99 \pm 0{\cdot}21$	$8{\cdot}61 \pm 0{\cdot}10$	$6{\cdot}36 \pm 0{\cdot}18$	$5{\cdot}93 \pm 0{\cdot}12$	$9{\cdot}7 \pm 0{\cdot}8$	$6{\cdot}59 \pm 0{\cdot}13$	$10{\cdot}10 \pm 0{\cdot}19$
$\Delta H°$/kJ mol^{-1} $\left(\text{assuming } \log \gamma_{\pm} = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+\sqrt{I}} - 0{\cdot}3I\right\}\right)$	$5{\cdot}53 \pm 0{\cdot}16$	$7{\cdot}67 \pm 0{\cdot}14$	$8{\cdot}22 \pm 0{\cdot}20$	$6{\cdot}15 \pm 0{\cdot}14$	$5{\cdot}72 \pm 0{\cdot}12$	$9{\cdot}2 \pm 0{\cdot}7$	$6{\cdot}36 \pm 0{\cdot}09$	$9{\cdot}66 \pm 0{\cdot}13$
$\Delta H°$/kJ mol^{-1} $\left(\text{assuming } \log \gamma_{\pm} = -2{\cdot}034\left\{\frac{\sqrt{I}}{1+\sqrt{I}} - 0{\cdot}2I\right\}\right)$ (ref. 35)	$5{\cdot}71 \pm 0{\cdot}17$		$8{\cdot}50 \pm 0{\cdot}17$	$5{\cdot}71 \pm 0{\cdot}09$		$9{\cdot}70 \pm 0{\cdot}25$ [g]	$6{\cdot}11 \pm 0{\cdot}15$	
Using log K (Izatt) and equation (8) $\overline{\Delta H}$ (calc.), this work	$2{\cdot}16 \pm 0{\cdot}33$	$3{\cdot}64 \pm 0{\cdot}15$	$2{\cdot}81 \pm 0{\cdot}36$	$2{\cdot}25 \pm 0{\cdot}11$	$1{\cdot}75 \pm 0{\cdot}15$	$5{\cdot}66 \pm 0{\cdot}22$	$2{\cdot}83 \pm 0{\cdot}20$	$4{\cdot}52 \pm 0{\cdot}23$
Reported values (ref. 3):	$2{\cdot}13 \pm 0{\cdot}13$	$3{\cdot}39 \pm 0{\cdot}34$	$2{\cdot}55 \pm 0{\cdot}04$	$2{\cdot}09 \pm 0{\cdot}09$	$1{\cdot}72 \pm 0{\cdot}08$	$5{\cdot}10 \pm 0{\cdot}13$	$2{\cdot}64 \pm 0{\cdot}08$	$4{\cdot}10 \pm 0{\cdot}17$

[a] Calorimetric data from refs. 3 and 34 for titration of $(Me_4N)_2SO_4$ into $M(ClO_4)_2$ solution. $\Delta H°$ calculated by conventional methods, a known value for $K°$ being assumed. Ref. 16. [c] Ref. 18. [d] Ref. 17. [e] Ref. 22. [f] Ref. 19. [g] Davies equation, $\beta = 0{\cdot}3$.

Because of the uncertainties associated with the $K°$ and $\Delta H°$ values determined by the 'entropy titration' method, $\Delta H°$ has been recalculated for the reactions $M^{2+} + SO_4^{2-} \rightleftharpoons MSO_4$ by using the best $K°$ values (from potentiometric or conductivity measurements) and the reported enthalpimetric titration data.[34] The programme was similar to that described previously [35] but replaced the approximate expression $\Delta H = \Delta H° + 6{\cdot}80 \log \gamma_{\pm}$ with the expression derived in this paper, $\Delta H = \Delta H° + 2[2{\cdot}303RT^2C'(I)]$; the results agree with those reported from direct calorimetric measurement (Table 3).

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[35] G. R. Hedwig and H. K. J. Powell, *J.C.S. Dalton*, 1973, 798.