568. *The Heat of Autoprotolysis of Sulphuric Acid.*

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In the molality range 0·06—0·09 the heat of the strong acid–strong base reaction

$$\mathrm{HB(HSO_4)_4}(m) + 2\mathrm{KHSO_4}(2\ \text{molal}) \longrightarrow \mathrm{KB(HSO_4)_4}(m) + \mathrm{KHSO_4}(m) + 2\mathrm{H_2SO_4}$$

in sulphuric acid solution is found to be $-5{\cdot}60 \pm 0{\cdot}04$ kcal. mole^{-1} at 25°. Corrections are considered for the calculation from this of the heat of autoprotolysis of the solvent, which is judged to be about 5 kcal. mole^{-1}, in satisfactory agreement with the earlier thermal estimate.[1] Values obtained by other methods are discussed.

The existing estimates of ΔH_{ap}, the heat of autoprotolysis of sulphuric acid, depend to varying extents upon assumptions made in the interpretation of the properties of the pure acid. There has been only one thermal determination of this quantity [1] and, since this has inspired little confidence [2,3] and has recently been criticized,[4] a discussion of the relative merits of the suggested values of ΔH_{ap} is called for. Calculations made upon the temperature dependence of the autoprotolysis constant, K_{ap}, will obviously need revision whenever the detailed interpretation of the constitution of the pure acid is revised: this is illustrated by the values (in kcal. mole^{-1}) 2 (ref. 5), (× 2, refs. 1, 4? but see ref. 3), 6·1 (ref. 3), and 3·4 (ref. 4), which have been derived from time to time in this way. The attraction of this type of calculation probably lies in the understandable conviction that because cryoscopic and conductance measurements are more precise near the pure acid composition than thermal measurements, final values of equilibrium constants should be based upon them. It would be inadvisable to suppose however that the latest detailed calculations made by Gillespie and his co-workers [4,6] are yet sufficiently acceptable to justify rejection of the only thermal estimate of ΔH_{ap} as 40% too high. (Kirkbride and Wyatt [1] obtained $\Delta H_{\mathrm{ap}} = 4{\cdot}8 \pm 0{\cdot}2$ kcal. mole^{-1}.) In particular, some doubt remains about the conductance treatment [7] and the description of dilute oleums.[8]

The principal assumption affecting the thermal determination [1] is that the concentrations of the autoprotolytic ions, $\mathrm{H_3SO_4^+}$ and $\mathrm{HSO_4^-}$, are equal in the pure solvent. Although an algebraic method was used in which ΔH_{ap} and K_{ap} were determined together, the actual value of $\Delta H_{\mathrm{ap}}/2$ (subject to this assumption) was determined within fairly narrow limits by the difference between the partial molar heat content of a metal hydrogen sulphate in the pure solvent and at a concentration of $\mathrm{HSO_4^-}$ great enough for effective suppression of the autoprotolysis. If it is established [6] that $m_{\mathrm{HSO_4^-}}$ exceeds $m_{\mathrm{H_3SO_4^+}}$ significantly in the pure acid, this calculation will require modification. However, the criticism by Gillespie, Robinson, and Solomons [4] placed the emphasis differently and could be misleading. They conclude that because some of the differences in the recorded relative $\bar{L}_2$ values (see ref. 1, Table 7) may be due to non-ideality,[1] neither K_{ap} nor ΔH_{ap} determined in this way need be taken seriously. But non-ideal $\bar{L}_2$ contributions large enough to affect these calculations would of course be reflected in the temperature dependence of activity coefficients and cast doubt upon the validity of simple calculations [6] at any temperature. The thermal values of ΔH_{ap} and K_{ap} are also stated [4] to be " inconsistent with the position of minimum conductivity," but this is an overstatement since these values are actually only inconsistent with a particular conductance interpretation, which is itself open to some criticism.[7]

[1] Kirkbride and Wyatt, *Trans. Faraday Soc.*, 1958, **54**, 483.
[2] Gillespie and Robinson, *Adv. Inorgan. Radiochem.*, 1959, p. 385.
[3] Greenwood and Thompson, *J.*, 1959, 3474.
[4] Gillespie, Robinson, and Solomons, *J.*, 1960, 4320.
[5] Gillespie and Wasif, *J.*, 1953, 964.
[6] Bass, Gillespie, and Robinson, *J.*, 1960, 821.
[7] Wyatt, *Trans. Faraday Soc.*, 1961, **57**, 773.
[8] Dacre and Wyatt, to be published.

In view of these uncertainties, we have devised a new thermal experiment, the results of which will lead to a more direct estimate of ΔH_{ap} through assumptions of a different kind. In principle it resembles the determination of ΔH_{ap} for water by a simple strong acid–strong base neutralization, but it is slightly complicated by a method for overcoming corrections due to the solvent autoprotolysis. In precise thermochemical terms, the heat of the following reaction is measured at 25° and expressed per mole of $HB(HSO_4)_4$:

$$HB(HSO_4)_4(m) + 2KHSO_4(2\text{ molal}) \longrightarrow KB(HSO_4)_4(m) + KHSO_4(m) + 2H_2SO_4 \quad . \; . \; . \quad (1)$$

$HB(HSO_4)_4$ being a strong acid [9] and $KHSO_4$ a strong base,[10] which is added to the acid in the form of a 2-molal solution in sulphuric acid. If only one equiv. of potassium hydrogen sulphate were added the reaction

$$H_3SO_4^+ + HSO_4^- \longrightarrow 2H_2SO_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

would not proceed to completion because of the solvent autoprotolysis in the " neutral " solution. The point of adding 2 equiv. is that the extent of solvent autoprotolysis should be approximately the same at the end of the experiment as at the beginning, so that complications due to the solvent autoprotolysis are eliminated. (If it transpires that the extent of autoprotolysis is not quite the same [6] at the same molality of strong acid and strong base, a slight correction can be made by interpolating to the base concentration at which the solvent effects are truly eliminated.)

Three determinations of ΔH for reaction (1) at different values of m (0·0630, 0·0825, 0·0901) gave a mean value of $-5{\cdot}60$ kcal. per mole of $HB(HSO_4)_4$. To convert this precise experimental value to $-\Delta H_{ap}$, three corrections must be considered:

(i) The acid $HB(HSO_4)_4$ may not be completely strong.[2,11] For this reason the molality was kept within the cryoscopic range,[9] although higher molalities would have reduced still further the importance of autoprotolytic effects. In this range cryoscopy shows that there can be no appreciable proportion of the acid un-ionized, so that any correction for this effect must be small. A similar assumption has been made in conductance work.[12]

(ii) A correction is necessary for (twice) that part of the heat of dilution of 2-molal potassium hydrogen sulphate which is not accounted for by the suppression of solvent autoprotolysis. According to ref. 1, this would be $-2 \times H_A = -2 \times 0{\cdot}1$ kcal. mole^{-1}; but some uncertainty arises from the fact that the new $\overline{H}_2$ values for the addition of potassium hydrogen sulphate to the " neutral " $KB(HSO_4)_4$ solution are rather greater than those for additions to the pure acid.[1] (This may expose a slight systematic error between the two investigations, possibly traceable to an uncertainty in fixing the composition of the pure acid. The $\overline{L}_2$ values relative to the " neutral " solvent, however, agree satisfactorily with those in Table 7 of ref. 1.) We conclude that the appropriate correction will probably not exceed $\pm 0{\cdot}2$ kcal. mole^{-1}.

(iii) The most important correction is that for solvolysis of the $H_3SO_4^+$ ion in the strong-acid solution,[9] although precise calculation here depends upon the theory adopted for dilute oleums. Our present view is that Gillespie and his co-workers have overestimated the concentration of un-ionized $H_2S_2O_7$ in the dilute oleum region and that this is the principal cause of the discrepancies in interpretation which have arisen. Calculations are still in progress and we merely record here that the correction in question will probably not exceed 0·6 kcal. mole^{-1}. In terms of the interpretation by Gillespie and his co-workers [4] on the other hand, the correction is completely calculable. We have merely to add to the heat of reaction (1) a fraction of the heat of the reaction

$$H_3SO_4^+ + H_2SO_4 \rightleftharpoons H_3O^+ + H_2S_2O_7 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

demanded by the equilibrium constant $K_{id}/K_a = 4{\cdot}2 \times 10^{-5}/0{\cdot}014$, *i.e.* 0·003 mole kg.$^{-1}$.

[9] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

[10] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1933, **55**, 1900.

[11] Flowers, Gillespie, and Robinson, *Canad. J. Chem.*, 1960, **38**, 1363.

[12] Flowers, Gillespie, Robinson, and Solomons, *J.*, 1960, 4327.

The heat of reaction (3) is $\Delta H_{id} - \Delta H_a$, *i.e.* 3·6 kcal. mole^{-1}, in their terms. The corrections become +0·6 to 0·7 kcal. mole^{-1}, depending upon the initial concentration of acid, so that in this way $\Delta H_{ap} = 5{\cdot}0 \pm 0{\cdot}2$ kcal. mole^{-1} would be calculated.

Confirmation that ΔH_{ap} must have approximately this value is also provided by the heat evolved per mole of HSO_4^- in the first additions to the acid. Thus, in the detailed example quoted in the experimental section, the first addition yields 4·98 kcal. mole^{-1}, but this requires correction for changes in the extents of autoprotolysis (+0·5 kcal. mole^{-1}) and $H_3SO_4^+$ solvolysis (*ca.* −0·1 kcal. mole^{-1}?) to give ΔH_{ap} (*ca.* 5·4 kcal. mole^{-1}).

Although the correction terms are clearly subject to revision, we conclude that the heat of reaction (1) provides a good guide to the magnitude of ΔH_{ap}, which must be approximately 5 kcal. mole^{-1}, within a few tenths of a kcal. mole^{-1}.

EXPERIMENTAL

The technique and apparatus for the thermal measurements have been described:[1] two Dewar flasks serve as twin calorimeters, one of which accommodates the reference junctions of the 20-junction copper–constantan thermel used for measuring the temperature changes. Into the main calorimeter were weighed about 1300 g. of a solution of known strength of tetra-(hydrogen sulphato)boric acid [9] in pure sulphuric acid. This was prepared by adding a weight of boric acid required to remove the (cryoscopically determined) excess of disulphuric acid in a dilute oleum according to the stoicheiometric equation

$$H_3BO_3 + 3H_2S_2O_7 \longrightarrow H_3SO_4^+ + B(HSO_4)_4^- + H_2SO_4 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Although the total heat of reaction (1) was principally required, the reaction was actually carried out in stages since the intermediate readings of $\overline{H}_2$ for HSO_4^- additions were also of interest. Details of the set of measurements for one experiment are given in the Table. In this case 1 g. of the added base solution contained 1·640 × 10^{-3} mole of potassium hydrogen sulphate. For each addition the value of $\overline{H}_2$, the partial molar heat content of potassium hydrogen sulphate relative to a 2-molal solution, is also recorded. Apart from the reference already made to this quantity, we note that this type of experiment permits $\partial\overline{H}_2/\partial m_2$ at zero (stoicheiometric) concentration of HSO_4^- to be estimated with greater confidence than is possible with additions to the pure solvent, where negative concentrations of HSO_4^- are not

Details of calculation for experiment 3.

HSO_4^- added (moles)	Moles (stoich.) ($H_3SO_4^+$)	Total H_2SO_4 (g.)	Heat evolved on addition (cal.)	Molality (stoich.) ($H_3SO_4^+$)	Mean molality during addn. ($H_3SO_4^+$)	$-\overline{H}_2$ rel. to 2m-$KHSO_4$ (kcal. mole^{-1})
—	0·1233	1369·3		0·0901		
			173·3		0·0769	4·98
0·0348	0·0885	1392·6		0·0636		
			164·2		0·0507	4·68
0·0351	0·0534	1416·7		0·0377		
			148·3		0·0255	4·33
0·0342	0·0192	1439·0		0·0133		
	(HSO_4^-)		100·5	(HSO_4^-)	0·0015	2·94
0·0342	0·0150	1458·9		0·0103	(HSO_4^-)	
			48·4		0·0195	1·78
0·0272	0·0422	1471·8		0·0287		
			25·8		0·0366	1·09
0·0236	0·0658	1482·0		0·0444		
			15·4		0·0517	0·69
0·0223	0·0881	1493·6		0·0590		
			9·7		0·0701	0·28
0·0346	0·1227	1510·2		0·0812		
			4·5		0·0919	0·13
0·0337	0·1564	1526·3		0·1025		

Total heat evolved up to addition of 2 × 0·1233 mole of HSO_4^- = 685·7 cal., whence $\Delta H(1) = -685{\cdot}7/0{\cdot}1233 = -5{\cdot}56$ kcal. mole^{-1}.

available.[13] The value of $(\partial\overline{H}_2/\partial m_2)_0$ for HSO_4^-, obtained graphically from the present result, is 65 kcal. mole^{-2} kg. ± 10%.

The three results for the overall heat of reaction (1) at 25° were: at initial $H_3SO_4,B(HSO_4)_4$ molality 0·0630, $\Delta H = -5{\cdot}59$ kcal. mole^{-1}; at 0·0825, $\Delta H = -5{\cdot}64$; at 0·0901, $\Delta H = -5{\cdot}56$. The mean value over the range 0·06—0·09 molal is therefore $-5{\cdot}60 \pm 0{\cdot}04$ kcal. mole^{-1}.

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[13] Wyatt, *Trans. Faraday Soc.*, 1956, **52**, 806.