

## Thermodynamics of Metal Complex Formation in Aqueous Solution. III. A Calorimetric Study of Hydrogen Sulphate and Uranium(VI) Sulphate, Acetate, and Thiocyanate Complexes

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The enthalpy changes for the formation of sulphate, acetate, and thiocyanate complexes of uranyl(VI) in an aqueous perchlorate medium of ionic strength 1.00 M have been determined calorimetrically at 25.00°C. By the same method, both the stability constant and the enthalpy change for the formation of hydrogen sulphate have also been determined. From the changes of enthalpy thus found, and the changes of free energy computed from the known stability constants, the changes of entropy have been calculated.

As has been stressed in the two preceding papers I and II of this series,<sup>1,2</sup> it is very important to know both the enthalpy and entropy changes for a reaction in order to obtain a good insight into the nature of the bond formed or disrupted. In Part II the determination of these quantities for the uranyl(VI) fluoride system has been reported. It seemed to be of interest to extend the investigation to other uranyl(VI) complexes, with donors softer than the fluoride ion. For this purpose, the sulphate and acetate systems, with oxygen as donor atom, and the thiocyanate system, with nitrogen as donor atom,<sup>3</sup> seemed suitable, especially as their stability constants have been measured previously.<sup>4-6</sup> This paper deals with the determination of the enthalpy changes,  $\Delta H_i^\circ$ , for the stepwise formation of complexes within these systems, carried out by direct calorimetric measurements. As discussed in Part II, this method of obtaining values of  $\Delta H_i^\circ$  is generally to be preferred to the temperature coefficient method. From the values of  $\Delta H_i^\circ$  found and those of  $\Delta G_i^\circ$  computed from the stability constants, the entropy changes  $\Delta S_i^\circ$  are calculated according to:

$$\Delta G_i^\circ = \Delta H_i^\circ - T \Delta S_i^\circ \quad (1)$$

The measurements refer to 25.00°C and a sodium perchlorate medium of unit ionic strength.

In order to avoid hydrolysis of the uranyl(VI) ion, perchloric acid has been added. When the donor atom is markedly basic, as is the case for the sulphate and, especially, for the acetate ion, proton as well as uranyl(VI) complexes are formed during the calorimetric experiments. In the thiocyanate system, this does not happen, as thiocyanic acid is quite a strong acid.<sup>7</sup> To find the heat changes referring to the formation of the uranyl(VI) complexes, those due to the formation, or disruption, of proton complexes has to be known. For this purpose,  $\Delta H_1^\circ$  for the formation of hydrogen sulphate has been determined in a separate investigation, while the value of  $\Delta H^\circ = -1.51 \text{ kJ mol}^{-1}$  for the formation of acetic acid under the present conditions has been taken from a compilation given in Ref. 8.

Very few determinations of  $\Delta H_i^\circ$  exist for the uranyl(VI) systems in question, and none of these is founded on calorimetric measurements. Day and Powers<sup>9</sup> have determined, by an extraction method, the stability constants of the uranyl(VI) sulphate system at 10, 25, and 40°C in a perchlorate medium of  $I=2 \text{ M}$ . From the temperature coefficients of  $\beta_1$  and  $\beta_2$ , they have found  $\Delta H_1^\circ = 10 \text{ kJ mol}^{-1}$  and  $\Delta H_2^\circ = -4 \text{ kJ mol}^{-1}$ . From measurements of the solubility of silver sulphate in uranyl sulphate solutions Lietzke and Stoughton<sup>10</sup> have determined  $\beta_1$  and  $\beta_2$  of the uranyl sulphate system in the temperature interval 25–200°C at zero ionic strength. From their temperature coefficients, a value of  $\Delta H_1^\circ$  between 10 and 22  $\text{kJ mol}^{-1}$  is calculated, while  $\Delta H_2^\circ$  is estimated to 4  $\text{kJ mol}^{-1}$ . Wallace<sup>11</sup> investigated the uranyl sulphate system by Donnan membrane equilibrium. He determined the stability constants at 25, 35, and 50°C at zero ionic strength. From these values he obtained  $\Delta H_1^\circ = 21 \text{ kJ mol}^{-1}$  and  $\Delta H_2^\circ = 8 \text{ kJ mol}^{-1}$ .

The hydrogen sulphate system, on the other hand, has repeatedly been studied by calorimetric measurements. Thus Zielen<sup>12</sup> has found  $\Delta H_1^\circ = 23.2 \text{ kJ mol}^{-1}$  at  $I=2.00 \text{ M}$  and 25°C. Austin *et al.*<sup>13</sup> and Christensen *et al.*<sup>14</sup> have determined  $\Delta H_1^\circ$  at  $I=0$  and 25°C. They reported  $\Delta H_1^\circ = 24.0 \text{ kJ mol}^{-1}$  and 23.4  $\text{kJ mol}^{-1}$ , respectively. The system has also been studied by the temperature coefficient method. From potentiometric measurements in the interval 10–75°C at  $I=1.0 \text{ M}$  Fletcher<sup>15</sup> calculated  $\Delta H_1^\circ = 22.6 \text{ kJ mol}^{-1}$  for 25°C.

*Calculation of enthalpy changes from calorimetric data.* The notation is the same as in Parts I and II in this series.<sup>1,2</sup>

The stability constants of the three uranyl systems have been determined at 20°C.<sup>4–6</sup> They have therefore to be recalculated to the temperature 25°C of the present study by the following iterative procedure. Values of  $\Delta H_i^\circ$  are first computed using the values of  $\beta_i$  valid for 20°C. By means of these approximate  $\Delta H_i^\circ$ ,  $\beta_i$  valid for 25°C were calculated according to

$$d \ln \beta_j / dT = \sum_{k=1}^j \Delta H_k^\circ / RT^2 \quad (2)$$

New values of  $\Delta H_i^\circ$  were obtained using these constants and so on. In fact, only one iteration had to be performed, as the differences between the  $\beta_j$ -values then computed and the "final" ones were less than one standard deviation. The constants valid for 25°C are collected in Table 7.

The calculation of the values of  $\Delta H_i^\circ$  from the experimental data has been described in paper II. Two different calculation methods have been used *viz.*

one graphical and one numerical. The latter, which is a least-squares procedure, has been developed by Sillén *et al.*<sup>16,17</sup> and uses a high speed computer. Within the limits of error stated, the same values of  $\Delta H_j^\circ$  were obtained by the two methods.

### EXPERIMENTAL

*Chemicals used.* The sodium sulphate (Merck's *p.a.*) stock solution was analyzed by (a) drying a sample and weighing the residue and (b) passing a sample through an ion exchange column in its acid form and titrating the eluate with standard sodium hydroxide. Both the methods gave concordant results.

*The acetate buffers* used were prepared from sodium acetate and acetic acid (Merck's *p.a.*) and were analyzed as described in Ref. 5.

*The sodium thiocyanate* (Baker's analyzed) stock solution was standardized by Volhard titration. All other chemicals used were prepared and analyzed as described in paper I.

*Procedure.* The calorimeter has been described in paper II. The measurements were performed as a series of titrations of a solution T into a calorimeter solution S. Every addition was 1–3 cm<sup>3</sup>. As before, two slightly different procedures have been used. Either portions of the solution were removed from the reaction vessel before each addition (scheme A) or after the vessel had been almost completely filled (scheme B).

The compositions of the solutions S and T are seen from Tables 1, 3, 5, and 6. Generally the solution S contained the central ion and T the ligand. For the two sulphate systems, however, some titrations have been carried out where the central ion has been added to a ligand solution.

The heats of dilution were determined by similar titrations, but with only one of the reactants present. Thus the heats of dilution for the solution S were determined by titrations with the solution T without the reactant, and for the solutions T analogously.

The heat equivalent,  $\varepsilon_V$ , which was obtained by electrical calibration, was found to obey the same equation as was reported in paper II.

Every titration series was usually repeated once and the reproducibility was in most cases within 0.05 J.

### MEASUREMENTS AND RESULTS

*The proton sulphate system.* The experimental data are given in Table 1. In all the five series performed the titration scheme B (see above) was used. Consequently, the total volume of the solution S was varied between 100.0 and 118.0 cm<sup>3</sup>. In the titration series a, b, and c, sodium sulphate solution was added to perchloric acid solutions (*cf.* Table 1). In order to check the reliability of the correction technique and to discover possible errors due to changes of the medium at the titrations, two series, d and e, were performed where solutions containing sodium sulphate were titrated with a perchloric acid solution.

In 1 M perchlorate medium, the hydrogen sulphate ion is so strong an acid that it becomes impossible to determine  $K$  very precisely by measurements of pH. It turns out that a much better value is obtained from the calorimetric measurements. Generally stability constants may be precisely determined in this way if (a) only one complex is formed, (b) the value of  $|\Delta H^\circ|$  is large, and (c) the value of  $K$  is not too large or too small.<sup>18,19</sup> These conditions are all well fulfilled for the proton sulphate system. For the calculations, the least-squares program "Letagrop Kalle" has been used. With this approach,  $\Delta H_1^\circ$  is calculated for a number of reasonable values of  $K_1$ . The combination, which gives the least standard deviation,  $\sigma Q'_{\text{corr}}$ , evidently represents the best fit with the experimental data. Corresponding values of  $K_1$  and  $\Delta H_1^\circ$  are collected in Table 2.

Table 1. Determination of the heats of formation for the proton sulphate complex.

For all series:  $V_0 = 100.0 \text{ cm}^3$  and  $V = (V_0 + v) \text{ cm}^3$ .

a<sup>I</sup> S:  $C_H = 0.1000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.900 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 13.782, 12.209, 0.092; 6.000, 12.711, 11.217, 0.038; 9.000, 11.698, 10.280, -0.002;  
12.000, 10.782, 9.443, 0.017; 15.000, 9.895, 8.627, -0.017;

a<sup>II</sup> S:  $C_H = 0.08696 \text{ M}$ ,  $C_L = 0.04370 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.783 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 8.987, 7.795, -0.058; 6.000, 8.155, 7.033, -0.059; 9.000, 7.410, 6.355, -0.046;  
12.000, 6.707, 5.720, -0.067; 15.000, 6.134, 5.213, -0.029;

b<sup>I</sup> S:  $C_H = 0.05000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.950 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 9.652, 8.079, 0.017; 6.000, 8.586, 7.092, 0.025; 9.000, 7.594, 6.176, -0.021; 12.000,  
6.799, 5.460, 0.020; 15.000, 6.050, 4.782, -0.008;

b<sup>II</sup> S:  $C_H = 0.04348 \text{ M}$ ,  $C_L = 0.04370 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.826 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 5.364, 4.171, -0.021; 6.000, 4.724, 3.602, -0.054; 9.000, 4.201, 3.146, -0.055;  
12.000, 3.711, 2.724, -0.100;

c<sup>I</sup> S:  $C_H = 0.02500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.975 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 6.389, 4.816, 0.008; 6.000, 5.502, 4.008, -0.013; 9.000, 4.774, 3.356, -0.033;  
12.000, 4.201, 2.862, -0.016; 15.000, 3.707, 2.439, -0.034;

c<sup>II</sup> S:  $C_H = 0.02174 \text{ M}$ ,  $C_L = 0.04370 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.848 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 3.264, 2.071, -0.042; 6.000, 2.895, 1.774, -0.029; 9.000, 2.586, 1.531, -0.025;

d<sup>I</sup> S:  $C_L = 0.05000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.850 \text{ M}$ .  
T:  $C_H = 0.4000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.600 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 9.514, 9.435, -0.109; 6.000, 8.326, 8.255, 0.050; 9.000, 7.230, 7.167, 0.108; 12.000,  
6.205, 6.150, 0.063; 15.000, 5.360, 5.314, 0.042;

d<sup>II</sup> S:  $C_H = 0.05217 \text{ M}$ ,  $C_L = 0.04348 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.817 \text{ M}$ .  
T:  $C_H = 0.4000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.600 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 4.644, 4.598, 0.054; 6.000, 3.983, 3.941, 0.055; 9.000, 3.448, 3.414, 0.054; 12.000,  
2.941, 2.912, -0.008; 15.000, 2.598, 2.573, 0.016;

Table 1. Continued.

d <sup>III</sup>	S: $C_H = 0.09754$ M, $C_L = 0.03781$ M, $C_{NaClO_4} = 0.789$ M. T: $C_H = 0.4000$ M, $C_{NaClO_4} = 0.600$ M.
$v/cm^3$ , $-Q_{exp}/J$ , $-Q'_{corr}/J$ , $\Delta Q'_{corr}/J$ :	3.000, 2.297, 2.276, 0.046; 6.000, 1.962, 1.946, 0.000; 9.000, 1.736, 1.724, 0.021; 12.000, 1.519, 1.510, 0.004;
e <sup>I</sup>	S: $C_L = 0.02500$ M, $C_{NaClO_4} = 0.925$ M. T: $C_H = 0.4000$ M, $C_{NaClO_4} = 0.600$ M.
$v/cm^3$ , $-Q_{exp}/J$ , $-Q'_{corr}/J$ , $\Delta Q'_{corr}/J$ :	3.000, 5.749, 5.653, -0.017; 6.000, 4.648, 4.561, -0.059; 9.000, 3.862, 3.782, -0.025; 12.000, 3.226, 3.155, -0.017; 15.000, 2.741, 2.678, 0.008;
e <sup>II</sup>	S: $C_H = 0.05217$ M, $C_L = 0.02174$ M, $C_{NaClO_4} = 0.883$ M. T: $C_H = 0.4000$ M, $C_{NaClO_4} = 0.600$ M.
$v/cm^3$ , $-Q_{exp}/J$ , $-Q'_{corr}/J$ , $\Delta Q'_{corr}/J$ :	3.000, 2.330, 2.276, 0.029; 6.000, 1.941, 1.891, 0.001; 9.000, 1.615, 1.573, -0.033; 12.000, 1.443, 1.406, 0.025;

Table 2. Values of  $\Delta H_1^\circ$  for the formation of  $HSO_4^-$  found for different values of  $K$ .

$K_1/M^{-1}$	$\Delta H_1^\circ/kJ\ mol^{-1}$	$\sigma Q'_{corr}/J$
15.0	$20.63 \pm 0.26$	0.165
14.0	$21.30 \pm 0.20$	0.126
13.0	$22.09 \pm 0.14$	0.087
12.0	$22.97 \pm 0.09$	0.053
11.8	$23.18 \pm 0.09$	0.049
11.6	$23.35 \pm 0.08$	0.046
11.5	$23.47 \pm 0.08$	0.045
11.4	$23.56 \pm 0.08$	0.045
11.2	$23.77 \pm 0.09$	0.047
11.0	$24.02 \pm 0.09$	0.050
10.0	$25.23 \pm 0.17$	0.089
9.0	$26.69 \pm 0.29$	0.143

The best fit, with  $\sigma Q'_{corr} = 0.045$  J, is obtained for  $K_1 = 11.5$  M<sup>-1</sup> and  $\Delta H_1^\circ = 23.5$  kJ mol<sup>-1</sup>. All the five titration series agree well as seen from Table 1, where  $\Delta Q'_{corr}$  is given for all points. The values of  $\Delta G_1^\circ$ ,  $\Delta H_1^\circ$ , and  $\Delta S_1^\circ$  are listed in Table 7.

*The uranyl(VI) sulphate system.* Six different titration series have been carried out all according to scheme B, Table 3. In the first three series (a-c) a sodium sulphate solution was added to uranyl(VI) perchlorate solutions of different  $C_M$  (and  $C_H$ ). In order to reach higher values of  $\bar{n}$  three titration series, d-f, were performed where solutions S of different sulphate buffers were titrated with a uranyl(VI) perchlorate solution.

Table 3. Determination of the heats of formation for the uranyl sulphate complexes.

For all the series:  $V_0 = 100.0 \text{ cm}^3$  and  $V = (V_0 + v) \text{ cm}^3$ .

a<sup>I</sup> ○ S:  $C_M = 0.03000 \text{ M}$ ,  $C_H = 0.01500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.895 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 13.477, 11.903, -0.088; 6.000, 12.067, 10.573, -0.004; 9.000, 10.594, 9.176, -0.042; 12.000, 9.288, 7.950, -0.034; 15.000, 8.067, 6.799, -0.100;

a<sup>II</sup> ○ S:  $C_M = 0.02609 \text{ M}$ ,  $C_L = 0.04370 \text{ M}$ ,  $C_H = 0.01304 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.778 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 7.037, 5.845, -0.067; 6.000, 6.071, 4.950, -0.084; 9.000, 5.293, 4.238, -0.075;  
12.000, 4.628, 3.640, -0.079; 15.000, 4.075, 3.155, -0.078;

a<sup>III</sup> ○ S:  $C_M = 0.02268 \text{ M}$ ,  $C_L = 0.08169 \text{ M}$ ,  $C_H = 0.01134 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.677 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 3.577, 2.720, -0.079; 6.000, 3.146, 2.351, -0.071; 9.000, 2.799, 2.063, -0.046;  
12.000, 2.494, 1.820, -0.029; 15.000, 2.243, 1.628, -0.008;

b<sup>I</sup> □ S:  $C_M = 0.02000 \text{ M}$ ,  $C_H = 0.01000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.930 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 11.632, 10.058, 0.071; 6.000, 9.728, 8.234, -0.002; 9.000, 8.159, 6.740, -0.013;  
12.000, 6.858, 5.519, -0.042; 15.000, 5.883, 4.615, -0.008;

b<sup>II</sup> □ S:  $C_M = 0.01739 \text{ M}$ ,  $C_L = 0.04370 \text{ M}$ ,  $C_H = 0.00870$ ,  $C_{\text{NaClO}_4} = 0.809 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 4.975, 3.782, -0.054; 6.000, 4.238, 3.117, -0.067; 9.000, 3.686, 2.632, -0.046;  
12.000, 3.197, 2.209, -0.071; 15.000, 2.824, 1.904, -0.054;

b<sup>III</sup> □ S:  $C_M = 0.01512 \text{ M}$ ,  $C_L = 0.08169 \text{ M}$ ,  $C_H = 0.00756 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.703 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 2.515, 1.657, -0.025; 6.000, 2.222, 1.427, -0.021;

c<sup>I</sup> △ S:  $C_M = 0.01000 \text{ M}$ ,  $C_H = 0.00500$ ,  $C_{\text{NaClO}_4} = 0.965 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 8.163, 6.590, 0.038; 6.000, 6.293, 4.799, 0.050; 9.000, 4.958, 3.540, -0.021; 12.000,  
4.071, 2.732, -0.029; 15.000, 3.452, 2.184, -0.020;

c<sup>II</sup> △ S:  $C_M = 0.00870 \text{ M}$ ,  $C_L = 0.04370 \text{ M}$ ,  $C_H = 0.00435 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.839 \text{ M}$ .  
T:  $C_L = 0.3350 \text{ M}$ .

$v/\text{cm}^3$ ,  $-Q_{\text{exp}}/J$ ,  $-Q'_{\text{corr}}/J$ ,  $\Delta Q'_{\text{corr}}/J$ :

3.000, 2.925, 1.732, -0.046; 6.000, 2.536, 1.414, -0.033; 9.000, 2.238, 1.184, -0.017;  
12.000, 1.971, 0.983, -0.029; 15.000, 1.787, 0.866, 0.000;

Table 3. Continued.

d<sup>I</sup> ● S:  $C_L = 0.3000$  M,  $C_H = 0.1500$  M,  $C_{NaClO_4} = 0.168$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 9.715, 9.021, 0.046; 6.000, 9.309, 8.661, 0.042; 9.000, 8.945, 8.343, 0.045; 12.000,  
8.531, 7.966, -0.004; 15.000, 8.226, 7.699, 0.046;

d<sup>II</sup> ● S:  $C_M = 0.01304$  M,  $C_L = 0.2609$  M,  $C_H = 0.1435$  M,  $C_{NaClO_4} = 0.224$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 7.786, 7.289, -0.038; 6.000, 7.368, 6.899, -0.062; 9.000, 7.025, 6.581, -0.054;  
12.000, 6.673, 6.255, -0.063; 15.000, 6.343, 5.945, -0.062;

d<sup>III</sup> ● S:  $C_M = 0.02439$  M,  $C_L = 0.2268$  M,  $C_H = 0.1378$  M,  $C_{NaClO_4} = 0.273$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 5.945, 5.565, -0.134; 6.000, 5.690, 5.326, -0.038; 9.000, 5.385, 5.033, -0.033;  
12.000, 5.042, 4.703, -0.075;

e<sup>I</sup> ■ S:  $C_L = 0.2000$  M,  $C_H = 0.07500$  M,  $C_{NaClO_4} = 0.309$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 10.016, 9.682, 0.013; 6.000, 9.652, 9.343, 0.121; 9.000, 9.192, 8.899, 0.092; 12.000,  
8.711, 8.439, 0.046; 15.000, 8.276, 8.021, 0.033;

e<sup>II</sup> ■ S:  $C_M = 0.01304$  M,  $C_L = 0.1739$  M,  $C_H = 0.07826$  M,  $C_{NaClO_4} = 0.347$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 7.820, 7.577, 0.012; 6.000, 7.351, 7.125, 0.004; 9.000, 6.920, 6.707, -0.004; 12.000,  
6.502, 6.301, -0.013; 15.000, 5.983, 5.791, -0.142;

e<sup>III</sup> ■ S:  $C_M = 0.02439$  M,  $C_L = 0.1512$  M,  $C_H = 0.08110$  M,  $C_{NaClO_4} = 0.380$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 5.686, 5.502, -0.050; 6.000, 5.314, 5.138, -0.021; 9.000, 4.954, 4.786, -0.012;  
12.000, 4.565, 4.406, -0.050;

f<sup>I</sup> ▲ S:  $C_L = 0.1500$  M,  $C_H = 0.05000$  M,  $C_{NaClO_4} = 0.484$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 9.795, 9.594, 0.192; 6.000, 9.272, 9.083, 0.196; 9.000, 8.699, 8.523, 0.117; 12.000,  
8.192, 8.025, 0.096; 15.000, 7.669, 7.514, 0.050;

f<sup>II</sup> ▲ S:  $C_M = 0.01304$  M,  $C_L = 0.1304$  M,  $C_H = 0.05652$  M,  $C_{NaClO_4} = 0.499$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 7.209, 7.063, 0.067; 6.000, 6.690, 6.552, 0.054; 9.000, 6.184, 6.054, 0.008; 12.000,  
5.720, 5.598, -0.017; 15.000, 5.343, 5.230, 0.016;

f<sup>III</sup> ▲ S:  $C_M = 0.02439$  M,  $C_L = 0.1134$  M,  $C_H = 0.06219$  M,  $C_{NaClO_4} = 0.512$  M.  
T:  $C_M = 0.1000$  M,  $C_H = 0.1000$  M,  $C_{NaClO_4} = 0.600$  M.  
 $v/cm^3$ ,  $-Q_{exp}/J$ ,  $-Q'_{corr}/J$ ,  $\Delta Q'_{corr}/J$ :  
3.000, 4.904, 4.799, -0.013; 6.000, 4.523, 4.422, 0.008; 9.000, 4.163, 4.071, 0.021; 12.000,  
3.803, 3.715, -0.004;

The part of  $Q'_{\text{corr}}$  referring to the formation of hydrogen sulphate has been calculated from the values of  $K_1$  and  $\Delta H_1^\circ$  obtained in the separate investigation of this complex.

The stability constants of the uranyl sulphate system have been determined according to two methods,<sup>4</sup> viz. potentiometrically and spectrophotometrically. These yielded somewhat different results. Within the range of  $[\text{L}]$  investigated, three complexes were indicated by the potentiometric method, but only two by the spectrophotometric one. As mentioned above it is sometimes possible to determine stability constants of high precision from calorimetric measurements. As at least two complexes are formed in rapid succession in the present system, the first condition for such a determination (p. 3679) is certainly not fulfilled. Therefore the prospects of making an independent determination of the values of  $\beta_i$  for the uranyl(VI) sulphate system by this method were not very good. Separate tests of the two sets of  $\beta_i$ -values reported in Ref. 4

Table 4. Values of  $\Delta H_i^\circ$  for the uranyl sulphate system found for different sets of  $\beta_i$ -values.

$i$	$\frac{\beta_i}{\text{M}^{-i}}$	$\sum_{k=1}^i \frac{\Delta H_k^\circ}{\text{kJ mol}^{-1}}$	$\frac{\sigma Q'_{\text{corr}}}{\text{J}}$	$\beta_i/\text{M}^{-i}$	$\sum_{k=1}^i \frac{\Delta H_k^\circ}{\text{kJ mol}^{-1}}$	$\frac{\sigma Q'_{\text{corr}}}{\text{J}}$
1	57	19.6 ± 0.5		60	19.0 ± 0.3	
2	440	34.8 ± 2.2	0.144	500	34.4 ± 1.1	0.089
3	3200	32.3 ± 2.7		1500	34.0 ± 3.3	
1	60	18.72 ± 0.20	0.074	64	18.23 ± 0.17	0.062
2	450	36.23 ± 0.43		570	35.11 ± 0.32	
1	60	18.67 ± 0.19	0.069	64	18.19 ± 0.19	0.070
2	510	35.20 ± 0.38		630	34.37 ± 0.34	
1	60	18.58 ± 0.23	0.082	70	17.78 ± 0.17	0.067
2	630	33.67 ± 0.38		500	37.47 ± 0.39	
1	64	18.28 ± 0.17	0.064	70	17.69 ± 0.17	0.062
2	510	36.02 ± 0.36		630	35.41 ± 0.31	

will show, however, which one that gives the best fit. Several combinations of  $\beta_1$  to  $\beta_3$  and  $\beta_1$  and  $\beta_2$ , respectively, where the values of  $\beta_i$  have been varied within the limits of error stated in Ref. 4, have been chosen for this test. Some of the results are listed in Table 4. If a value of  $\beta_3$  of the order of magnitude found in the potentiometric investigation is applied, the fit achieved with three complexes is not at all as good as with two complexes. As to the approach with two complexes, several sets of constants give about the same fit. The original values of Ahrlund,<sup>4</sup> valid for 20°C, yield when recalculated to 25°C  $\beta_1 = 64 \text{ M}^{-1}$  and  $\beta_2 = 570 \text{ M}^{-2}$ . These are used in the further calculations as no other set gives a significantly better fit. Corresponding values of  $\Delta G_i^\circ$ ,  $\Delta H_i^\circ$ , and  $\Delta S_i^\circ$  have been collected in Table 7. In Fig. 1,  $\Delta h_v$  has been plotted as a



Table 5. Determination of the heats of formation for the uranyl acetate complexes.

For all the series:  $V_0 = 100.0 \text{ cm}^3$  and  $V = (V_0 + v) \text{ cm}^3$ .

a<sup>I</sup> ○ S:  $C_M = C_H = 0.05000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.815 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, 7.853, 1.205; 6.000, 6.464, 0.218; 9.000, 2.841, -3.075; 12.000, -3.059, -8.678;  
14.000, -3.724, -7.360; 16.000, -3.883, -7.431;

a<sup>II</sup> ○ S:  $C_M = 0.04310 \text{ M}$ ,  $C_L = 0.4138 \text{ M}$ ,  $C_H = 0.3879 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.722 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, -5.146, -10.150; 6.000, -4.121, -8.832; 9.000, -3.012, -7.460; 12.000, -1.904,  
-6.117; 15.000, -0.782, -4.812;

a<sup>III</sup> ○ S:  $C_M = 0.03748 \text{ M}$ ,  $C_L = 0.7512 \text{ M}$ ,  $C_H = 0.6634 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.737 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, 0.473, -3.389; 6.000, 1.703, -2.013; 9.000, 2.561, -1.029;

b<sup>I</sup> ◇ S:  $C_M = 0.03000 \text{ M}$ ,  $C_H = 0.06000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.850 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, 8.326, 1.678; 6.000, 7.640, 1.393; 9.000, 6.130, 0.213; 12.000, 1.916, -3.703; 14.000,  
-1.908, -5.544; 16.000, -2.761, -6.309;

b<sup>II</sup> ◇ S:  $C_M = 0.02586 \text{ M}$ ,  $C_L = 0.4138 \text{ M}$ ,  $C_H = 0.3966$ ,  $C_{\text{NaClO}_4} = 0.802 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, -3.648, -8.653; 6.000, -2.188, -6.899; 9.000, -0.506, -4.954; 12.000, 1.159,  
-3.054; 15.000, 2.506, -1.523;

b<sup>III</sup> ◇ S:  $C_M = 0.02249 \text{ M}$ ,  $C_L = 0.7511 \text{ M}$ ,  $C_H = 0.6709 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.763 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, 3.268, -0.594;

c<sup>I</sup> □ S:  $C_M = 0.03000 \text{ M}$ ,  $C_H = 0.03000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.880 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, 7.640, 0.992; 6.000, 3.121, -3.125; 8.000, -2.234, -6.251; 10.000, -3.042,  
-6.912; 13.000, -3.686, -9.226; 16.000, -2.163, -7.489;

c<sup>II</sup> □ S:  $C_M = 0.02586 \text{ M}$ ,  $C_L = 0.4138 \text{ M}$ ,  $C_H = 0.3707 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.828 \text{ M}$ .  
T:  $C_L = 3.000 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
3.000, -0.573, -5.577; 6.000, 1.117, -3.594; 9.000, 2.590, -1.858; 12.000, 3.494,  
-0.720; 15.000, 3.782, -0.247;

d<sup>I</sup> ■ S:  $C_M = 0.03000 \text{ M}$ ,  $C_H = 0.01000 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.900 \text{ M}$ .  
T:  $C_L = 3.003 \text{ M}$ ,  $C_H = 2.500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/J$ ,  $Q'_{\text{corr}}/J$ :  
2.000, 1.941, -2.594; 4.000, -3.492, -7.832; 6.000, -3.428, -7.598; 8.000, -2.581,  
-6.598; 10.000, -1.756, -5.627; 13.000, -1.327, -6.870; 16.000, 0.089, -5.234;

Table 5. Continued.

d<sup>II</sup> ■ S:  $C_M = 0.02586$  M,  $C_L = 0.4142$  M,  $C_H = 0.3534$  M,  $C_{NaClO_4} = 0.845$  M.  
T:  $C_L = 3.003$  M,  $C_H = 2.500$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
3.000, 1.751, -3.251; 6.000, 3.175, -1.536; 9.000, 3.879, -0.569; 12.000, 4.106, -0.109;

e<sup>I</sup> △ S:  $C_M = 0.01500$  M,  $C_H = 0.01500$  M,  $C_{NaClO_4} = 0.940$  M.  
T:  $C_L = 3.000$  M,  $C_H = 2.500$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
2.000, 4.841, 0.305; 4.000, 0.146, -4.192; 5.000, -1.021, -3.146; 6.000, -0.795, -2.879;  
8.000, -0.757, -4.774; 10.000, 0.364, -3.506; 13.000, 2.469, -3.071; 16.000, 4.033,  
-1.293;

e<sup>II</sup> △ S:  $C_M = 0.01293$  M,  $C_L = 0.4138$  M,  $C_H = 0.3578$  M,  $C_{NaClO_4} = 0.879$  M.  
T:  $C_L = 3.000$  M,  $C_H = 2.500$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
3.000, 4.636, -0.368;

f<sup>I</sup> ▲ S:  $C_M = 0.01500$  M,  $C_H = 0.00500$  M,  $C_{NaClO_4} = 0.950$  M.  
T:  $C_L = 3.003$  M,  $C_H = 2.500$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
2.000, -0.928, -5.464; 4.000, -1.820, -6.159; 6.000, -0.514, -4.686; 8.000, 0.542,  
-3.477; 10.000, 1.589, -2.284; 13.000, 4.032, -1.510; 16.000, 4.729, -0.594;

f<sup>II</sup> ▲ S:  $C_M = 0.01293$  M,  $C_L = 0.4142$  M,  $C_H = 0.3491$  M,  $C_{NaClO_4} = 0.888$  M.  
T:  $C_L = 3.003$  M,  $C_H = 2.500$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
3.000, 4.873, -0.130;

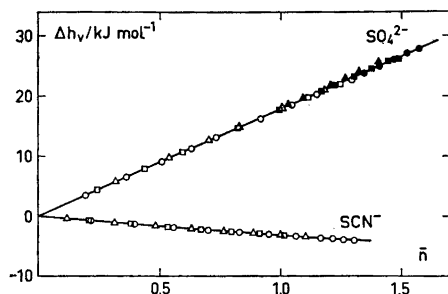
g<sup>I</sup> ● S:  $C_M = 0.05000$  M,  $C_H = 0.01000$  M,  $C_{NaClO_4} = 0.840$  M.  
T:  $C_L = 1.503$  M,  $C_H = 1.000$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
2.000, -1.996, -2.937; 4.000, -8.560, -9.468; 6.000, -8.724, -9.598; 8.000, -7.686,  
-8.527; 10.000, -6.690, -7.502; 13.000, -8.502, -9.652; 16.000, -7.050, -8.138;

g<sup>II</sup> ● S:  $C_M = 0.04310$  M,  $C_L = 0.2073$  M,  $C_H = 0.1466$  M,  $C_{NaClO_4} = 0.793$  M.  
T:  $C_L = 1.503$  M,  $C_H = 1.000$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
3.000, -5.607, -6.636; 6.000, -4.322, -5.297; 9.000, -3.079, -4.004; 12.000, -1.983,  
-2.862; 15.000, . . . . ., precipitation.

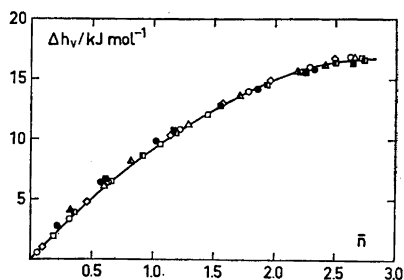
h<sup>I</sup> ■ S:  $C_M = 0.03000$  M,  $C_H = 0.01000$  M,  $C_{NaClO_4} = 0.900$  M.  
T:  $C_L = 1.503$  M,  $C_H = 1.000$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
2.000, -0.732, -1.674; 4.000, -7.849, -8.757; 6.000, -7.364, -8.238; 8.000, -5.812,  
-6.653; 10.000, -4.648, -5.460; 13.000, -5.268, -6.418; 16.000, -3.556, -4.644;

h<sup>II</sup> ■ S:  $C_M = 0.02586$  M,  $C_L = 0.2073$  M,  $C_H = 0.1466$  M,  $C_{NaClO_4} = 0.845$  M.  
T:  $C_L = 1.503$  M,  $C_H = 1.000$  M,  $C_{NaClO_4} = 0.500$  M.  
 $v/cm^3$ ,  $Q_{exp}/J$ ,  $Q'_{corr}/J$ :  
3.000, -1.962, -2.992; 6.000, -0.494, -1.469; 9.000, 0.439, -0.485; 12.000, 0.812,  
-0.067;

function of  $\bar{n}$ . The function is independent of  $C_M$  which proves that no polynuclear complexes exist (*cf.* the acetate system). The full drawn curve has been calculated from the enthalpy changes and stability constants given in Table 7.



*Fig. 1.* The total molar enthalpy change,  $\Delta h_v$ , as a function of  $\bar{n}$ , for the uranyl(VI) sulphate and thiocyanate systems, *cf.* Tables 3 and 6. Only half of the experimental points, chosen at random, have been plotted.



*Fig. 2.* The total molar enthalpy change,  $\Delta h_v$ , as a function of  $\bar{n}$ , for the uranyl(VI) acetate system, *cf.* Table 5. Only half of the experimental points, chosen at random, have been plotted.

*The uranyl(VI) acetate system.* Even in acetate buffers containing a large proportion of acetic acid, the value of pH is high enough to cause a hydrolysis of the uranyl(VI) ion. This hydrolysis decreases rapidly, however, as the formation of acetate complexes proceeds. At high concentration of acetate the hydrolysis is virtually suppressed even in buffers containing a fairly low proportion of acid.<sup>5</sup>

The initial hydrolysis which involves the formation of polynuclear complexes may exert a considerable influence on  $Q'_{\text{corr}}$ . It is therefore necessary to know the range within which such reactions occur. For this purpose, the acidity and the central ion concentration should be varied. Calorimetric titrations of this system have therefore been performed with two buffers of different acidity *viz.* with  $[\text{HAc}] : [\text{Ac}^-]$  equal to 5 : 1 and 2 : 1, respectively. The values of  $C_M$  and  $C_H$  of the solutions S have also been varied. All the titrations have been carried out according to the scheme B, see Table 5. The heats of dilution for the two buffers used were substantial, up to 2.2 J per cm<sup>3</sup> added solution T for the 5 : 1 buffer and up to 0.5 J for the 2 : 1 buffer.

To correct for the formation of acetic acid, it was necessary to know  $K$  and  $\Delta H^\circ$  for this reaction under the prevailing conditions. The following values were used:<sup>5,8</sup>  $K = 3.84 \times 10^4 \text{ M}^{-1}$ ,  $\Delta H^\circ = -1.51 \text{ kJ mol}^{-1}$ .

The experimental data are collected in Table 5 and the  $\Delta h_v$ -functions are plotted *versus*  $\bar{n}$  in Fig. 2, where the full drawn curve has been calculated from the enthalpy changes and stability constants quoted in Table 7. The titration series performed with the 2 : 1 buffer deviate progressively as  $[\text{L}]$  decreases. The deviation becomes significant for  $\bar{n} < 1.3$ . In the same region a slight divergence can also be observed for those titrations with the 5 : 1 buffer,

where the initial value of  $C_H$  is especially low. These discrepancies are evidently due to the hydrolytic reactions occurring in this range. For all the series, the  $\Delta h_v$ -curves are expected to coincide at high values of  $\bar{n}$  as the hydrolysis is likely to become suppressed by the formation of the uranyl acetate complexes. As shown by the graph, this is generally the case. The scattering observed is probably due to errors in the corrections for the heats of dilution.

Measurements with various  $C_M$  gave the same  $\Delta h_v$ -curve, when hydrolysis could be neglected. This confirms that no polynuclear acetate complexes exist in the solutions.

The values of  $\Delta G_i^\circ$ ,  $\Delta H_i^\circ$  and  $\Delta S_i^\circ$  with their estimated errors are listed in Table 7.

*The uranyl thiocyanate system.* Titrations were performed according to the scheme A, i.e. the volume  $V$  is a constant ( $=100.24 \text{ cm}^3$ ), Table 6. As the complex formation is rather weak and the values of  $|\Delta H_i^\circ|$  small, it was necessary to use high values of  $C_M$  in order to get reasonably high values of  $Q'_{\text{corr}}$ . Consequently,  $C_M$  could not be varied very much, but within the limitations thus imposed no sign of polynuclear complexes was found.

Table 6. Determination of the heats of formation for the uranyl thiocyanate complexes.

For all the series:  $V = V_0 = 100.24 \text{ cm}^3$ .

a     $\circ$     S:  $C_M = 0.07071 \text{ M}$ ,  $C_H = 0.0500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.738 \text{ M}$ .  
T:  $C_{\text{NaSCN}} = 1.000 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/\text{J}$ ,  $Q'_{\text{corr}}/\text{J}$ ,  $\Delta Q'_{\text{corr}}/\text{J}$ :

3.000, 2.106, 2.510, 0.054; 6.000, 1.872, 2.255, 0.012; 9.000, 1.692, 2.054, -0.025; 12.000, 1.532, 1.870, -0.055; 15.000, 1.333, 1.657, -0.013; 18.000, 1.186, 1.490, -0.004; 21.000, 1.066, 1.356, -0.008; 24.000, 0.956, 1.226, 0.000; 27.000, 0.846, 1.100, 0.012; 30.000, 0.754, 0.996, 0.017; 33.000, 0.684, 0.912, 0.009; 36.000, 0.607, 0.828, 0.009; 39.000, 0.541, 0.753, 0.008; 42.000, 0.480, 0.686, 0.004; 45.000, 0.438, 0.636, -0.008; 48.000, 0.415, 0.602, -0.029; 51.000, 0.380, 0.565, -0.046; 54.000, 0.344, 0.523, -0.055; 57.000, 0.312, 0.481, -0.054;

b     $\square$     S:  $C_M = 0.07071 \text{ M}$ ,  $C_H = 0.0500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.738 \text{ M}$ .  
T:  $C_{\text{NaSCN}} = 0.950 \text{ M}$ ,  $C_{\text{HClO}_4} = 0.0500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/\text{J}$ ,  $Q'_{\text{corr}}/\text{J}$ ,  $\Delta Q'_{\text{corr}}/\text{J}$ :

3.000, 2.001, 2.427, 0.008; 6.000, 1.795, 2.197, -0.030; 9.000, 1.556, 1.933, 0.004; 12.000, 1.415, 1.770, -0.021; 15.000, 1.232, 1.569, 0.009; 18.000, 1.115, 1.435, -0.004; 21.000, 0.993, 1.297, 0.005; 24.000, 0.876, 1.163, 0.021; 27.000, 0.808, 1.084, -0.004; 30.000, 0.724, 0.987, -0.005; 33.000, 0.619, 0.870, 0.029; 36.000, 0.560, 0.803, 0.017; 39.000, 0.518, 0.753, -0.008; 42.000, 0.455, 0.678, 0.000;

c     $\triangle$     S:  $C_M = 0.05303 \text{ M}$ ,  $C_H = 0.0500 \text{ M}$ ,  $C_{\text{NaClO}_4} = 0.791 \text{ M}$ .  
T:  $C_{\text{NaSCN}} = 0.952 \text{ M}$ ,  $C_{\text{HClO}_4} = 0.0500 \text{ M}$ .

$v/\text{cm}^3$ ,  $Q_{\text{exp}}/\text{J}$ ,  $Q'_{\text{corr}}/\text{J}$ ,  $\Delta Q'_{\text{corr}}/\text{J}$ :

3.000, 1.523, 1.950, 0.004; 6.000, 1.345, 1.745, -0.029; 9.000, 1.160, 1.536, -0.017; 12.000, 0.982, 1.339, 0.016; 15.000, 0.879, 1.218, 0.000; 18.000, 0.787, 1.109, -0.008; 21.000, 0.715, 1.017, -0.021; 24.000, 0.593, 0.883, 0.021; 27.000, 0.497, 0.770, 0.050; 30.000, 0.419, 0.682, 0.063; 33.000, 0.403, 0.657, 0.021; 36.000, 0.351, 0.594, 0.021; 39.000, 0.312, 0.544, 0.013; 42.000, 0.284, 0.510, -0.004; 45.000, 0.246, 0.464, -0.004;

A new set of stability constants has been calculated from Ahrland's measurements<sup>6</sup> by Sillén and Warnqvist.<sup>20</sup> It was investigated whether these values would give a better fit than the original ones. However, the same good fit,  $\sigma Q'_{\text{corr}} \approx 0.030$  J, was obtained in both cases. The calorimetric measurements are thus equally well interpreted with both sets. For the further calculations, the original values have been adopted. The results are collected in Table 7. It can be mentioned that the set of constants reported by Sillén and Warnqvist<sup>20</sup> gives almost the same value of  $\Delta H_1^\circ$  ( $= -3.30$  kJ mol<sup>-1</sup>), while the values of  $\Delta H_2^\circ$  ( $= -3.1$  kJ mol<sup>-1</sup>) and  $\Delta H_3^\circ$  ( $= -4.4$  kJ mol<sup>-1</sup>) are considerably different from those given in Table 7. As only small amounts of the second and third complexes are formed during the titrations, the values of  $\Delta H_2^\circ$  and  $\Delta H_3^\circ$  are not very precise anyhow. In Fig. 1 the  $\Delta h_v$ -function is plotted versus  $\bar{n}$ . The fulldrawn curve is calculated from the stability constants and enthalpy changes listed in Table 7.

## DISCUSSION

In Table 7, the values of  $\Delta G_j^\circ$ ,  $\Delta H_j^\circ$ , and  $\Delta S_j^\circ$  for the systems investigated have been collected. The limits of error stated refer either to three standard deviations, as given by the computer, or to maximum errors estimated from the graphical evaluation.

Table 7. The stability constants used and the computed values of  $\Delta G_j^\circ$ ,  $\Delta H_j^\circ$ , and  $\Delta S_j^\circ$  for the stepwise reactions of the systems investigated. The errors given correspond to three standard deviations or to estimated errors.

System →		H <sup>+</sup> - SO <sub>4</sub> <sup>2-</sup>	UO <sub>2</sub> <sup>2+</sup> - SO <sub>4</sub> <sup>2-</sup>	UO <sub>2</sub> <sup>2+</sup> - Ac <sup>-</sup>	UO <sub>2</sub> <sup>2+</sup> - NCS <sup>-</sup>
$\beta_j/M^{-j}$	$j=1$	11.5 ± 0.5	64 ± 6	263 ± 10	5.6 ± 0.3
	2		570 ± 60	(2.6 ± 0.2)10 <sup>4</sup>	5.2 ± 1.0
	3			(2.5 ± 0.3)10 <sup>6</sup>	15 ± 5
$\frac{-\Delta G_j^\circ}{\text{kJ mol}^{-1}}$	1	6.05 ± 0.10	10.31 ± 0.24	13.81 ± 0.09	4.27 ± 0.14
	2		5.42 ± 0.40	11.39 ± 0.21	-0.2 ± 0.7
	3			11.31 ± 0.35	2.6 ± 1.2
$\frac{-\Delta H_j^\circ}{\text{kJ mol}^{-1}}$	1	-23.47 ± 0.25	-18.23 ± 0.17	-10.54 ± 0.10	3.22 ± 0.06
	2		-16.88 ± 0.36	-9.67 ± 0.20	5.7 ± 0.6
	3			4.0 ± 0.4	-2.9 ± 1.0
$\frac{\Delta S_j^\circ}{\text{J mol}^{-1}\text{K}^{-1}}$	1	99.0 ± 0.9	95.7 ± 1.0	81.7 ± 0.5	3.5 ± 0.5
	2		74.8 ± 1.8	70.6 ± 1.0	-19.8 ± 3.0
	3			24.5 ± 1.8	18 ± 5

The value of  $K_1$  found here for the hydrogen sulphate system agrees very well with that obtained in the same medium by Ramette and Stewart<sup>21</sup> by a solubility method. They report, for 25°C,  $K_1 = 10.9$  M<sup>-1</sup>. The potentiometric measurements of Ahrland and Brandt<sup>22</sup> in the same medium yielded, at 20°C,

$K_1 = (13.0 \pm 1.5) \text{ M}^{-1}$ , corresponding to  $15 \text{ M}^{-1}$  at  $25^\circ\text{C}$ . By the same method Vdovenko *et al.*<sup>23</sup> have determined  $K_1$  in perchlorate media of various ionic strength and temperature. For  $25^\circ\text{C}$  and  $I = 1.0 \text{ M}$  they found  $K_1 = (13.3 \pm 0.7) \text{ M}^{-1}$ .

The value of  $\Delta H_1^\circ$  obtained for the proton sulphate formation agrees very well with the values quoted on p. 3678, in spite of the large differences in ionic strength between the various measurements (*cf.* Ref. 2).

The value of  $\Delta H_1^\circ$  found for the uranyl sulphate system is compatible with the approximate results reported (p. 3678), while the value of  $\Delta H_2^\circ$  is much more endothermic than has been found previously.

For the uranyl(VI) thiocyanate system our value of  $\Delta H_1^\circ$  is slightly exothermic. Bale *et al.*<sup>24</sup> have determined  $\beta_1$  of the same system in 20 % methanol at  $15 - 45^\circ\text{C}$  by spectrophotometric measurements. From the variation of  $\beta_1$  with  $T$  they found  $\Delta H_1^\circ = 4.8 \text{ kJ mol}^{-1}$ , *i.e.* slightly endothermic. The difference of medium in the two cases may be the main reason for the discrepancy.

The sulphate and acetate ions are oxygen donors and should consequently be looked upon as rather hard ligands. In agreement with the general rule for hard-hard interactions,<sup>25</sup> the reactions between these ligands and the two hard acceptors  $\text{H}^+$  and  $\text{UO}_2^{2+}$  are characterized by highly positive entropy changes. Furthermore they are all endothermic, with the exception of the third step in the uranyl(VI) acetate system, which is weakly exothermic.

According to Fronæus and Larsson,<sup>3</sup> the thiocyanate ion is bonded to the uranyl(VI) ion *via* the nitrogen atom, which is classified as a considerably softer donor than oxygen. In accordance with this we have found small values of  $\Delta H_i^\circ$  and  $\Delta S_i^\circ$  for the uranyl(VI) thiocyanate system, with no regular trend.

The large positive values of  $\Delta H_i^\circ$  and  $\Delta S_i^\circ$  for the formation of the sulphate complexes of  $\text{UO}_2^{2+}$  and  $\text{H}^+$  indicate that these species are inner sphere complexes.<sup>26</sup>

Further discussion will be postponed until the complete result of this investigation has been reported.

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