Thermodynamics of Metal Complex Formation in Aqueous Solution. IV. Equilibrium and Enthalpy Measurements on the Zinc and Mercury(II) Thiocyanate Systems

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The enthalpy changes accompanying the formation of zinc and mercury(II) thiocyanate complexes have been determined calorimetrically. For the zinc system, a redetermination of the stability constants has also been performed. From the changes of enthalpy measured, and the changes of free energy computed from the stability constants, the changes of entropy have been calculated. All data refer to 25.0°C and an aqueous sodium perchlorate medium of ionic strength 1.00 M.

Especially the first two mercury complexes are very strong which is due to a highly negative enthalpy term while the entropy term is counteracting the complex formation. For the weak zinc complexes, the enthalpy, as well as the entropy terms, are all small.

The previous papers I–III of this series [1-3] have mainly dealt with the changes of free energy, enthalpy, and entropy accompanying the formation of a number of uranyl(VI) complexes in aqueous solution. The changes of free energy, ΔG_j°, have been computed from the stability constants while the changes of enthalpy, ΔH_j°, have been measured calorimetrically. Finally, the changes of entropy, ΔS_j°, have been obtained from the relation

$$\Delta G_j^\circ = \Delta H_j^\circ - T\Delta S_j^\circ$$

It is also of great interest to study how these functions vary when complexes are formed between a certain ligand and central ions of different types. Among the ligands used in the previous investigations, the thiocyanate ion is very suitable for such a comparison, as it forms complexes with a great variety of acceptors. An especially interesting group to study in this connexion should be the divalent ions of electron configuration d^{10}, *viz.* Zn^{2+}, Cd^{2+}, and Hg^{2+}, as they show such a striking variation in their bonding properties,[4] from the distinctly hard Zn^{2+} to the very soft Hg^{2+}.

Table 1. Comparison of reported values of stability constants and enthalpy changes for the zinc and mercury(II) thiocyanate systems.

System	Zn²⁺ – SCN⁻							Hg²⁺ – SCN⁻			
Ref.	6	7	8	9	10	14	15	16	17	18	19
Temp./°C	25		30		20	25	40	25	25	25	25
I/M and medium	4 LiClO$_4$		2 KNO$_3$	varying	1 NaClO$_4$	$I \to 0$		1 NaClO$_4$	1 NaClO$_4$	0.2 KNO$_3$	$I \to 0$
β_j/M^{-j} $j=1$	13	5.4	3	8.2	0.5	71		1.20×10^{9}			
$\quad\quad\quad\quad$ 2	65	13.5	7		6			7.2×10^{16}	1.18×10^{16}	2.7×10^{16}	
$\quad\quad\quad\quad$ 3	640	5	1		2			5.0×10^{19}	8.9×10^{18}	1.39×10^{19}	
$\quad\quad\quad\quad$ 4	630	36	20		8		55	4.7×10^{21}	8.7×10^{20}	1.32×10^{21}	7.8×10^{21}
$-\sum_{k=1}^{j} \Delta H_k^\circ$ kJ mol^{-1} 1						-0.9					
$\quad\quad\quad\quad$ 2										125	
$\quad\quad\quad\quad$ 3										121	
$\quad\quad\quad\quad$ 4							24			150	150

The thiocyanate system of Cd^{2+} has been very thoroughly investigated by Gerding and Johansson,[5] while the data available for the Zn^{2+} and Hg^{2+} systems are rather sparse, Table 1. This especially applies to the values of $\Delta H°$ which are moreover mostly determined from the temperature coefficients of the stability constants, a method which usually does not yield very reliable results.[2] An investigation of these systems therefore seemed strongly motivated.

Like the previous investigations in this series,[1-3] the present one was performed at 25.0°C and in an aqueous medium of unit ionic strength with sodium perchlorate as supplementary electrolyte.

The stability constants of the zinc thiocyanate system have previously been determined by several methods: potentiometrically,[6] polarographically,[7,8] spectrophotometrically,[9] and by extraction,[10] Table 1. The results do not agree very well, however. The complexes are no doubt very weak. Potentiometric measurements of the central ion concentration should therefore offer a good method for the determination of their stability.[11] Such measurements can be carried out by means of the zinc amalgam electrode which has been shown to work very well if oxygen is rigorously excluded.[12,13]

A value of $\Delta H_1°$ at $I = 0$ for the zinc thiocyanate system has been determined calorimetrically by Nancollas and Torrance [14], Table 1. From the temperature dependence of β_4 Golub and Ivanchenko [15] have calculated a value of $\Delta H_4°$.

For the mercury(II) thiocyanate system the stability constants determined potentiometrically by Ciavatta and Grimaldi [16] have been used, Table 1. These refer to the same conditions as have been chosen for our measurements.

The constants K_3 and K_4 have also been determined from solubility data by the same authors.[16] The values found agree excellently with those found potentiometrically. Also the values of K_3 and K_4 determined polarographically by Nyman and Alberts [17] for the same medium agree very well with the two sets presented by Ciavatta and Grimaldi,[16] Table 1. On the other hand, the value of β_2 found by Nyman and Alberts is markedly lower than that found potentiometrically. As far as $\Delta H_1°$ and $\Delta H_2°$ are concerned this difference does not matter as the reactions are in any case stoichiometrically complete, but the values of $\Delta S_1°$ and $\Delta S_2°$ will be somewhat different dependent upon the value of β_2 chosen.

The constants have also been determined polarographically by Tanaka et al.[18] in 0.2 M KNO_3, Table 1. In spite of the difference of medium, the results agree fairly well with those mentioned above.
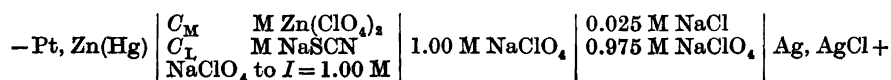
Tanaka et al.[18] have measured the constants also at 15 and 35°C and the values of $\Delta H_j°$ found are listed in Table 1. A value of $\sum_{j=1}^{4} \Delta H_j°$ has also been determined by Toropova [19] from the variation of β_4 with T.

CALCULATIONS

The notation is the same as in papers I – III of this series.[1-3]

Calculation of stability constants from potentiometric measurements of the free central ion concentration. The method of calculation has been described in Refs. 11 and 20. Only a short summary is therefore given here.

The emf of the following cell

$$-\text{Pt, Zn(Hg)} \left| \begin{array}{l} C_M \quad \text{M Zn(ClO}_4)_2 \\ C_L \quad \text{M NaSCN} \\ \text{NaClO}_4 \text{ to } I = 1.00 \text{ M} \end{array} \right| 1.00 \text{ M NaClO}_4 \left| \begin{array}{l} 0.025 \text{ M NaCl} \\ 0.975 \text{ M NaClO}_4 \end{array} \right| \text{Ag, AgCl}+$$

can be written as

$$E = e_{RE} - e_0 - RT/2F \cdot \ln[M] = E_k - RT/2F \cdot \ln[M] \tag{1}$$

where e_{RE} = electrode potential of the reference half-cell (including liquid junction potentials) and e_0 = standard potential of the $Zn^{2+}/Zn(Hg)$ electrode. The difference E_k is a constant.

Assuming only mononuclear complexes, the following relation holds

$$X([L]) = C_M/[M] = 1 + \sum_{j=1}^{N} \beta_j[L]^j \tag{2}$$

From eqns. (1) and (2) we arrive at

$$E_M = (RT/2F)\ln(C_M/[M]) = (RT/2F)\ln X([L]) \tag{3}$$

where E_M is the difference between the emf, E, of the cell above and the emf, E_0, of the same cell with $C_L = 0$, i.e. $[M] = C_M$.

By determining E_M as a function of C_L for a number of different C_M and extrapolating to $C_M = 0$, the value of E_M and thus X (according to eqn. (3)) can be determined as a function of $(C_L)_{C_M=0} = [L]$. Hence the mononuclear constants β_j can be found by established methods.

If only mononuclear complexes are present, the value of the ligand number $\bar{n} = (C_L - [L])/C_M$ will be equal to the slope, k, of the straight $(C_L - C_M)$-lines of constant E_M used for the extrapolation to $C_M = 0$, as in that case [L], and also

$$\bar{n} = \bar{n}_0 = \sum_{j=1}^{N} j\beta_j[L]^j/X \tag{4}$$

are constant along each line, as is evident from eqns. (2) and (3). If, on the other hand, polynuclear complexes also exist, this will no longer be true. The lines will not necessarily be straight and their slopes in the points ([L], 0) of interception with the C_L-axis will be $< \bar{n}_0$. It is thus possible to get information about the existence of polynuclear complexes by comparing the slopes, k, with the values of $\bar{n}_0$ obtained from eqn. (4).

The ligand number $\bar{n}$ for the mononuclear complexes can also be calculated from the function $E_M([L])$ according to the Bodländer equation:[21]

$$\bar{n} = \frac{\Delta E_M}{(RT/2F)\Delta \ln [L]} \tag{5}$$

A $\bar{n}$-value obtained by eqn. (5) is ascribed to the geometric mean of the two [L]-values in question.

The calculation of the enthalpy changes from the calorimetric measurements has been performed as before,[2,3] i.e. two methods, one graphical and one numerical, have been used. The numerical method uses a least-squares computer program, "Letagrop Kalle".[22,23]

EXPERIMENTAL

Chemicals. Zinc perchlorate was prepared by dissolving zinc oxide (Baker *p.a.*) in perchloric acid. In order to avoid hydrolysis, a small excess of the acid was used.[14] The zinc concentration was determined by titration with EDTA using Erio-T as an indicator. In the stock solution C_M was found to be 333.7 mM. In the same solution, a value of $h \approx 5$ mM was found by potentiometric titrations with sodium hydroxide.

Mercury(II) perchlorate was prepared by dissolving a weighed amount of HgO (Merck *p.a.*) in a known excess of $HClO_4$. As a check, the mercury(II) concentration was determined by thiocyanate titration, with Fe^{3+} as an indicator.[15]

Zinc amalgam was prepared and stored as described by Persson.[13] The amalgam is extremely sensitive to oxidation, and air had therefore to be completely excluded. The amalgam contained about 2.5 % zinc. The exact concentration is not critical as, at 25°C, two phases are formed between 2.18 and 45 %.[26]

All other chemicals used were prepared and analyzed as before.[1-3]

The potentiometric measurements. The emfs of the cells were measured to ± 0.01 mV by a digital voltmeter (DM 2022). The Ag,AgCl electrodes were prepared according to Brown.[27] For the solution in the left-hand half-cell, an electrode vessel of the Ingold type was used, with a tight fitting lid. The cell was kept in a water thermostat, at 25.0 ± 0.1°C.

The measurements were arranged as titrations. The solutions in the left-hand half-cell were obtained by adding a volume v cm³ of a solution T to $V_0 = 15.00$ cm³ of a solution S, where S and T had the compositions:

$$S: \begin{cases} C_M & M \ Zn(ClO_4)_2 \\ (1.00 - 3C_M) & M \ NaClO_4 \end{cases} \qquad T: 1.000 \ M \ NaSCN$$
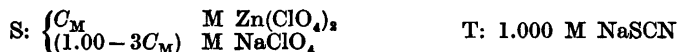
At every point during the titrations C_M and C_L were known from the compositions of the S and T solutions. As the T-solution did not contain any zinc ions, C_M continuously decreased as C_L increased. The difference between the emf, E, at a certain point and the initial emf, E_0', was therefore due to dilution, as well as to the formation of complexes. To find the difference E_M, defined in eqn. (3) as due only to the formation of complexes, the following correction was applied.

The initial emf, E_0', is given by (*cf.* eqn. (1))

$$E_0' = E_k - (RT/2F)\ln C_M' \qquad (6)$$

After the addition of v cm³ of the solution T to V_0 cm³ of the solution S, the total concentration of the metal ions has been reduced:

$$C_M = C_M' V_0/(v + V_0) \qquad (7)$$

Hence

$$E_0' = E_k - (RT/2F)\ln C_M - (RT/2F)\ln[(V_0 + v)/V_0] = E_0 - (RT/2F)\ln[(V_0 + v)/V_0] \qquad (8)$$

and

$$E_M = E - E_0 = E - E_0' - (RT/2F)\ln[(V_0 + v)/V_0] \qquad (9)$$

Before the solutions S and T were used a stream of purified nitrogen was bubbled through them in order to remove every trace of oxygen. Before entering the solutions, the nitrogen was bubbled through 1 M $NaClO_4$ to obtain the correct pressure of water vapour. During the titrations, nitrogen was also passed through the solution in the electrode vessel. In this way, a good mixing was also obtained. The nitrogen left the electrode vessel through a water-trap.

All titration series were repeated at least once and the reproducibility was in general within 0.04 mV at low values of C_L and within 0.1 mV at high values. The potentials attained equilibrium in less than 5 min.

The calorimetric measurements. The calorimeter and the technique of measurement have been described previously.[2] As before, two somewhat different titration procedures were used. Either portions of the solution were removed from the reaction vessel before each addition of titrant T (scheme A) or after the vessel had been almost completely filled (scheme B). The compositions of the solutions S and T are given in Tables 3 and 4.

In order to determine the corrections due to the heats of dilution, series were performed, which were analogous to those of the main measurements, except that only one of the two reactants was present simultaneously.

Electrical calibration showed that the heat equivalent was the same linear function of the volume of titrant added as has been found before.

The titration series were repeated once and the reproducibility was generally within 0.05 J.

MEASUREMENTS AND RESULTS

Stability constants of the zinc thiocyanate. As a check that the zinc amalgam electrode behaved according to Nernst's law, the emf's, E_0, for cells without ligand present were measured as a function of $C_M = [M]$ (p. 3695). These measurements were also arranged as titrations where a solution S (p. 3696) was titrated with 1.00 M $NaClO_4$. The E_k-value calculated from eqn. (1) was found to be constant within ± 0.05 mV for 2 mM $\le [M] \le 45$ mM.

The series with ligand present were performed with four different values of C_M. Corresponding values of C_L and E_M from these series are collected in Table 2. The graphical evaluation indicated four mononuclear complexes, with stability constants listed in Table 5.

The complex formation function, $\bar{n}([L])$, computed from this set of constants according to eqn. (4) is given in Fig. 1 as a fulldrawn curve. The values of $\bar{n}$ obtained from eqn. (5) agree very well with this curve. On the other

Table 2. Corresponding values of C_L and E_M for the zinc thiocyanate system.

| $C_M'/\text{mM}\rightarrow$	6.66	13.32	26.68	44.50
C_L/mM	E_M/mV			
32.3	2.03	2.00	1.89	1.78
62.5	3.91	3.82	3.65	3.42
90.9	5.64	5.56	5.29	4.98
117.6	7.24	7.14	6.81	6.48
142.9	8.77	8.64	8.28	7.92
166.7	10.21	10.05	9.65	9.24
189.2	11.58	11.40	10.96	10.50
210.5	12.85	12.67	12.21	11.69
230.8	14.06	13.85	13.40	12.87
250.0	15.19	15.00	14.50	13.96
268.3	16.30	16.06	15.56	15.03
285.7	17.33	17.09	16.58	16.05
302.3	18.31	18.05	17.54	17.03
318.2	19.24	18.99	18.47	17.95
333.3	20.13	19.89	19.36	18.84
347.8	20.95	20.75	20.21	19.69
375.0	22.52	22.30	21.78	21.24
400.0	23.98	23.72	23.26	22.71
423.1	25.31	25.08	24.65	24.05
444.4	26.50	26.27	25.89	25.30
464.3	27.61	27.38	27.00	26.41
482.8	28.60	28.39	28.03	27.46
500.0	29.53	29.32	28.87	28.43
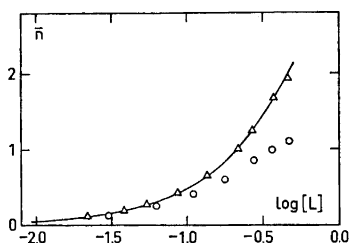
Fig. 1. The complex formation function of the zinc thiocyanate system. The full-drawn curve has been computed from eqn. (4) while the symbols ($\triangle$) refer to $\bar{n}$ found by means of eqn. (5). The values of k obtained from the slopes of the (C_M, C_L)-lines are denoted by (O). ([L] in M).
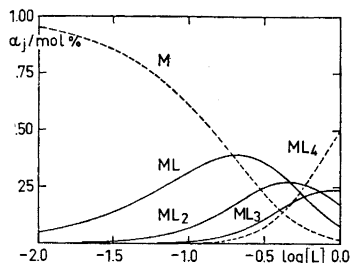

Fig. 2. The distribution of zinc between the different complexes, ML_j, at varying thiocyanate concentration, [L] (in M).

hand, the slopes k from the (C_M, C_L)-lines (p. 3695) differ considerably from the values of $\bar{n}$ calculated from eqns. (4) and (5), Fig. 1. The discrepancy is most marked at high values of $\bar{n}$. The effect is probably due to changes in the activity coefficients brought about by complex formation and by the progressive exchange of ClO_4^- for SCN^- during the titrations. In view of the small potential differences which give rise to the effect observed, it seems hazardous to interpret it as due to a formation of polynuclear complexes.

Enthalpy changes of the zinc thiocyanate. Eight different titration series have been carried out, Table 3. In four of these, a-d, ligand was added to a solution of the metal ion, according to the scheme A. With this arrangement, values of [L] high enough to bring about a sizable formation of the third and fourth complexes could not be reached, on account of their low stabilities. Higher values of [L] could be reached, however, by adding a metal solution T to a ligand solution S. This was done in the last four series, which were performed according to the scheme B.

In order to prevent hydrolysis in the zinc solutions,[24] these always contained a small amount of perchloric acid ($C_H : C_M \approx 0.01$) but since thiocyanic acid is very strong,[28] this does not imply any formation of undissolved acid during the titrations. In Fig. 3, the Δh_v-function is plotted *versus* $\bar{n}$. Evidently, Δh_v is independent of C_M, in spite of the fairly large variation of C_M during the experiments. This proves that no polynuclear species are formed, *i.e.* the interpretation given to the potentiometric measurements is substantiated.

With the stability constants reported above, a good fit, $\sigma Q'_{corr} = 0.034$ J, was obtained. The results are collected in Table 5. Other sets of reasonably chosen constants,[3] including three as well as four complexes, did not give any significantly better fit.

Enthalpy changes of the mercury(II) thiocyanate. Four different series were performed according to the scheme A, Table 4. The mercury(II) solutions had to be highly acidic in order to avoid hydrolysis,[29] but no formation of thiocyanic acid would occur.[28]

Table 3. Determination of the heats of formation for the zinc thiocyanate complexes.

For the series a−d: $V = V_0 = 100.24$ cm³ and for the series e−h:
$V_0 = 100.0$ cm³ and $V = (V_0 + v)$ cm³.

a   O   S: $C_M = 0.06674$ M, $C_{NaClO_4} = 0.800$ M.
                  T: $C_{NaSCN} = 1.000$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 3.650, 4.084, −0.004; *6.000*, 3.169, 3.582, 0.038; *9.000*, 2.755, 3.146, 0.020; *12.000*, 2.440, 2.812, −0.004; *15.000*, 2.153, 2.506, −0.025; *18.000*, 1.909, 2.243, 0.005; *21.000*, 1.694, 2.013, 0.039; *24.000*, 1.538, 1.837, 0.009; *27.000*, 1.405, 1.690, 0.011; *30.000*, 1.321, 1.594, −0.012; *33.000*, 1.161, 1.418, 0.032; *36.000*, 1.084, 1.331, 0.012; *39.000*, 0.993, 1.230, 0.029; *42.000*, 0.886, 1.109, 0.058; *45.000*, 0.832, 1.046, 0.035;

b   □   S: $C_M = 0.03307$ M, $C_{NaClO_4} = 0.900$ M.
                  T: $C_{NaSCN} = 1.000$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 1.939, 2.377, −0.032; *6.000*, 1.585, 1.996, −0.015; *9.000*, 1.352, 1.745, −0.033; *12.000*, 1.084, 1.456, 0.029; *15.000*, 0.986, 1.339, −0.017; *18.000*, 0.886, 1.218, −0.030; *21.000*, 0.781, 1.096, −0.040; *24.000*, 0.641, 0.941, 0.022; *27.000*, 0.604, 0.891, −0.003; *30.000*, 0.536, 0.808, −0.001; *33.000*, 0.524, 0.782, −0.040; *36.000*, 0.466, 0.711, −0.021; *39.000*, 0.433, 0.669, −0.033; *42.000*, 0.357, 0.582, 0.003; *45.000*, 0.352, 0.565, −0.021; *48.000*, 0.329, 0.536, −0.032;

c   △   S: $C_M = 0.02668$ M, $C_{NaClO_4} = 0.920$ M.
                  T: $C_{NaSCN} = 1.000$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 1.459, 1.895, 0.017; *6.000*, 1.177, 1.586, 0.040; *9.000*, 0.979, 1.372, 0.028; *12.000*, 0.813, 1.184, 0.041; *15.000*, 0.713, 1.067, 0.019; *18.000*, 0.597, 0.929, 0.026; *21.000*, 0.541, 0.858, 0.007; *24.000*, 0.496, 0.795, −0.003; *27.000*, 0.450, 0.736, −0.022; *30.000*, 0.347, 0.619, 0.036; *33.000*, 0.343, 0.602, 0.006; *36.000*, 0.298, 0.544, 0.014; *39.000*, 0.273, 0.506, 0.006; *42.000*, 0.254, 0.477, −0.002; *45.000*, 0.182, 0.397, 0.043; *48.000*, 0.182, 0.385, 0.019;

d   ▽   S: $C_M = 0.01669$ M, $C_{NaClO_4} = 0.950$ M.
                  T: $C_{NaSCN} = 1.000$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 0.788, 1.222, 0.015; *6.000*, 0.643, 1.054, 0.001; *9.000*, 0.487, 0.879, 0.021; *12.000*, 0.375, 0.745, 0.042; *15.000*, 0.317, 0.669, 0.020; *18.000*, 0.268, 0.602, 0.006; *21.000*, 0.240, 0.556, −0.001; *24.000*, 0.189, 0.490, 0.007; *27.000*, 0.165, 0.452, 0.001; *30.000*, 0.130, 0.402, 0.016; *33.000*, 0.117, 0.377, 0.003; *36.000*, 0.091, 0.339, 0.013; *39.000*, 0.070, 0.305, 0.019; *42.000*, 0.068, 0.293, −0.001; *45.000*, 0.019, 0.234, 0.041;

e   ●   S: $C_{NaSCN} = 0.8000$ M, $C_{NaClO_4} = 0.200$ M.
                  T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 2.883, 3.217, −0.070; *6.000*, 2.682, 2.962, 0.064; *9.000*, 2.636, 2.874, 0.037;

f   ■   S: $C_{NaSCN} = 0.6000$ M, $C_{NaClO_4} = 0.400$ M.
                  T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 2.489, 2.720, −0.032; *6.000*, 2.343, 2.540, 0.019; *9.000*, 2.276, 2.448, −0.012;

g   ▲   S: $C_{NaSCN} = 0.5000$ M, $C_{NaClO_4} = 0.500$ M.
                  T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
3.000, 2.197, 2.385, 0.009; *6.000*, 2.088, 2.243, 0.023; *9.000*, 2.021, 2.151, −0.004;

h   ▼   S: $C_{NaSCN} = 0.4000$ M, $C_{NaClO_4} = 0.600$ M.
                  T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:
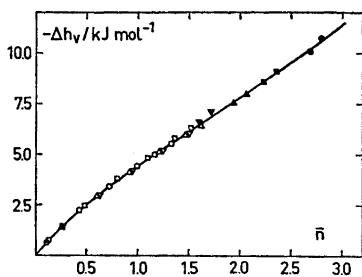*3.000*, 1.975, 2.142, −0.090; *6.000*, 1.828, 1.962, −0.029; *9.000*, 1.749, 1.837, −0.012;

Fig. 3. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the zinc thiocyanate system, cf. Table 3. Only half of the experimental points, chosen at random, have been plotted.
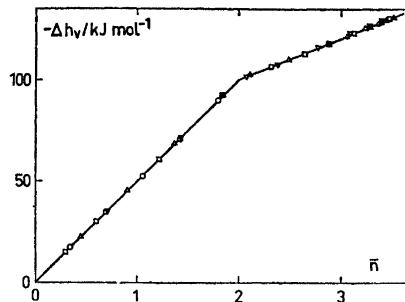

Fig. 4. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the mercury(II) thiocyanate system, cf. Table 4.

Table 4. Determination of the heats of formation for the mercury(II) thiocyanate complexes.

For all the series: $V = V_0 = 100.24$ cm³.

a   O   S: $C_M = 0.005903$ M, $C_H = 0.200$ M, $C_{NaClO_4} = 0.782$ M.
            T: $C_{NaSCN} = 0.1000$ M, $C_{NaClO_4} = 0.900$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:

2.000, 9.852, 9.924, −0.028; *4.000*, 9.862, 9.933, 0.067; *6.000*, 9.871, 9.945, 0.055; *8.000*, 9.960, 10.033, 0.024; *10.000*, 10.013, 10.088, −0.015,........precipitation.

b   □   S: $C_M = 0.003378$ M, $C_H = 0.200$ M, $C_{NaClO_4} = 0.787$ M.
            T: $C_{NaSCN} = 0.1000$ M, $C_{NaClO_4} = 0.900$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:

1.000, 4.985, 5.021, −0.079; *2.000*, 4.954, 4.987, 0.018; *4.000*, 9.918, 9.987, 0.027; *6.000*, 10.051, 10.121, −0.046; *8.000*, 4.305, 4.376, 0.020; *10.000*, 1.945, 2.017, −0.007; *12.000*, 1.405, 1.477, −0.016; *15.000*, 1.403, 1.510, −0.040; *18.000*, 0.852, 0.958, −0.014; *21.000*, 0.511, 0.619, 0.019; *24.000*, 0.325, 0.431, 0.023;

c   △   S: $C_M = 0.003378$ M, $C_H = 0.200$ M, $C_{NaClO_4} = 0.787$ M.
            T: $C_{NaSCN} = 0.1000$ M, $C_{NaClO_4} = 0.900$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:

1.500, 7.438, 7.494, −0.031; *3.000*, 7.450, 7.502, −0.002; *4.500*, 7.485, 7.540, −0.057; *6.000*, 7.499, 7.552, 0.031; *7.000*, 3.180, 3.213, −0.027; *9.000*, 2.223, 2.297, 0.046; *12.000*, 2.276, 2.385, 0.002; *14.000*, 0.995, 1.067, −0.012; *17.000*, 0.950, 1.059, 0.029; *20.000*, 0.593, 0.699, 0.024; *23.000*, 0.353, 0.460, 0.045; *26.000*, 0.217, 0.326, 0.041;

d   ▽   S: $C_M = 0.001417$ M, $C_H = 0.200$ M, $C_{NaClO_4} = 0.796$ M.
            T: $C_{NaSCN} = 0.1000$ M, $C_{NaClO_4} = 0.900$ M.

v/cm³, Q_{exp}/J, Q'_{corr}/J, $\Delta Q'_{corr}$/J:

1.000, 4.952, 4.987, −0.017; *2.000*, 5.015, 5.050, −0.035; *3.000*, 4.100, 4.134, 0.034; *4.000*, 0.794, 0.828, −0.014; *6.000*, 1.065, 1.134, −0.065; *9.000*, 0.810, 0.912, −0.052; *12.000*, 0.378, 0.481, 0.000; *15.000*, 0.196, 0.297, 0.007;

As $Hg(SCN)_2$ is precipitated at $\bar{n} \approx 2$ even for rather low values of C_M (cf. series a), no great variation of C_M has been possible, but within the concentration ranges used, no polynuclear complexes are indicated, see Fig. 4. The graphical and numerical methods of calculation gave concordant values of ΔH_j°. The results are collected in Table 5. The standard deviation, $\sigma Q'_{corr}$, was 0.035 J. The values of $\Delta Q'_{corr}$ for all individual points are included in Table 4.

DISCUSSION AND CONCLUSIONS

Our values of β_j for the zinc thiocyanate system (Table 5) agree fairly well with those reported by Saraiya and Sundaram[7] (Table 1). On the whole, they are also compatible with the set found by Frank and Hume,[8] and with

Table 5. The stability constants used and the computed values of ΔG_j°, ΔH_j° and ΔS_j° for the stepwise reactions of the zinc, cadmium and mercury(II) thiocyanate systems. The data for the cadmium system are taken from Ref. 5. The errors given correspond to three standard deviations or to estimated errors.

Metal		Zn^{2+}	Cd^{2+}	Hg^{2+}
β_j/M^{-j}	$j=1$	5.10 ± 0.03	20.7 ± 0.5	$(1.20 \pm 0.09) \times 10^{9}$
	2	11.0 ± 0.6	97 ± 5	$(7.2 \pm 0.9) \times 10^{16}$
	3	15.0 ± 3.6	107 ± 20	$(5.0 \pm 1.2) \times 10^{19}$
	4	32 ± 5	75 ± 30	$(4.7 \pm 0.3) \times 10^{21}$
$\dfrac{-\Delta G_j^{\circ}}{kJ\ mol^{-1}}$	1	4.04 ± 0.02	7.53 ± 0.08	51.83 ± 0.17
	2	1.91 ± 0.14	3.85 ± 0.08	44.41 ± 0.34
	3	0.76 ± 0.6	0.3 ± 0.7	16.2 ± 0.6
	4	1.87 ± 0.8	-0.9 ± 1.6	11.2 ± 0.7
$\dfrac{-\Delta H_j^{\circ}}{kJ\ mol^{-1}}$	1	5.80 ± 0.15	9.58 ± 0.04	49.73 ± 0.27
	2	1.8 ± 1.0	8.08 ± 0.38	50.43 ± 0.45
	3	0.8 ± 3.0	9.2 ± 3.8	20.4 ± 0.7
	4	7.7 ± 3.5		21.0 ± 1.3
$\dfrac{\Delta S_j^{\circ}}{J\ mol^{-1}\ K^{-1}}$	1	-5.9 ± 0.5	-6.7 ± 0.4	7.0 ± 1.1
	2	0 ± 4	-14 ± 1.3	-20.2 ± 1.9
	3	0 ± 10	-30 ± 13	-14 ± 3
	4	-19 ± 12		-33 ± 5

the value of β_1 found by Fronæus and Larsson.[9] The values reported by Mironov et al.[6] seem on the other hand much too large, and those of Tribalat and Dutheil[10] rather too small to be consistent with our results.

Our value of ΔH_1° for this system, -5.8 kJ mol^{-1}, is considerably different from that found at $I = 0$ by Nancollas and Torrance,[14] 0.9 kJ mol^{-1}. Similarly for the cadmium thiocyanate system, the value of $\Delta H_1^{\circ} = -9.58$ kJ mol^{-1} found by Gerding and Johansson[5] at $I = 1$ is much more negative than the

value of -2.9 kJ mol^{-1} found by Nancollas and Torrance [14] at $I = 0$. It is still an open question whether these differences are due only to the difference in ionic medium, especially as ΔH_1° of the cadmium thiocyanate system [5] does not vary at all between $I = 2$ and $I = 0.25$ M.

The value of $\sum_{k=1}^{4} \Delta H_k^\circ = -150$ kJ mol^{-1} for the mercury(II) thiocyanate reported by Tanaka et al.[18] and by Toropova [19] agrees fairly well with our value of -141 kJ mol^{-1}. In this case, the temperature coefficient method thus yields an acceptable result, which is not unexpected in view of the large value of $\sum_{k=1}^{4} \Delta H_k^\circ$ which implies a strong variation of β_4 with T. The individual values of ΔH_j° are nevertheless not nearly as precisely determined as by the calorimetric method.

The softness of the acceptors involved in the thiocyanate measurements decreases in the sequence [4] $Hg^{2+} \gg Cd^{2+} > Zn^{2+} > UO_2^{2+}$. According to the general rule, the complex formation reactions should then become less exothermic (or more endothermic) in this sequence. As seen from Table 5, and Table 7 of Ref. 3, this is generally the case. Especially the difference between the very soft Hg^{2+} and the border line acceptor Cd^{2+} is, as expected, very large, but a quite marked difference also exists between Cd^{2+} and the hard acceptors Zn^{2+} and UO_2^{2+}. The difference between these is on the other hand not very significant.

The entropy changes are small, and they vary in a rather irregular manner between the systems, and between consecutive steps within each system. As may be expected, however, the values become on the whole more negative with increasing softness of the acceptor.[4]

The thiocyanate ion possesses two different donor atoms, viz. the softer S, preferred by soft acceptors, and the harder N, preferred by hard acceptors. As to the present acceptors, Hg^{2+} certainly coordinates via S, and Zn^{2+} and UO_2^{2+} via N, while Cd^{2+} presumably has much the same affinity to both donor atoms.[30]

Contrary to thiocyanate complexes, complexes formed by typically hard ligands are always heavily entropy stabilized while the enthalpy term is generally positive and thus counteracting the reaction, often strongly so.[4] As has already been pointed out,[2,3] this general rule has been amply confirmed by the present investigations, comprising the fluoride complexes [2] of H^+, VO^{2+}, and UO_2^{2+}, the sulphate complexes [3] of H^+ and UO_2^{2+}, and the acetate complexes [3] of UO_2^{2+}.

Both for H^+ and UO_2^{2+}, the fluoride complexes are formed in much less endothermic reactions than the sulphate complexes while the entropy change is much the same for corresponding steps. This seems moreover to be a general rule, as judged from the analogous behaviour displayed by other acceptors as diverse as In^{3+}, Y^{3+}, and Th^{4+}, Table 6. The rule applies both to the first and second step of complex formation. The higher stability of the fluoride complexes is thus exclusively due to a less unfavourable enthalpy change.

It has been stated [31] that "the more negative (or less positive) ΔH°, the stronger is generally the covalent bonding". The application of this rule

Table 6. Comparison of the thermodynamics of fluoride and sulphate complexes (ΔG_j°, ΔH_j° in kJ mol^{-1} and ΔS_j° in J mol^{-1} K^{-1}).

	I/M	F$^-$			SO$_4$$^{2-}$			Ref.
		$-\Delta G_1^\circ$	$-\Delta H_1^\circ$	ΔS_1°	$-\Delta G_1^\circ$	$-\Delta H_1^\circ$	ΔS_1°	
H$^+$ {	1	16.86	-12.17	97.4	6.05	-23.5	99.0	2, 3
	0	18.11	-13.31	105.4	11.34	-24.0	118.8	4, 31
UO$_2$$^{2+}$	1	25.89	-1.70	92.5	10.31	-18.23	95.7	2, 3
	2				7.03	-16.90	80.3	32
Y^{3+} {	0.5	22.34	-9.2	105				33
	0	27.32	-9.6	125	19.08	-15.10	114.6	33, 34
In^{3+}	0	26.36	-14.6	138	17.36	-29.1	156	31, 34
Th^{4+} {	2				18.79	-20.92	133.5	35
	0	48.16	5.0	145^a				36
		$-\Delta G_2^\circ$	$-\Delta H_2^\circ$	ΔS_2°	$-\Delta G_2^\circ$	$-\Delta H_2^\circ$	ΔS_2°	
UO$_2$$^{2+}$	1	19.65	-0.40	67.2	5.42	-16.88	74.8	2, 3
Th^{4+} {	2				13.81	-19.46	111.7	35
	0	37.8	3.3	115 ^{a}				36

^{a} These values are calculated from the values of ΔH_j° and logK_j found by Baumann.[36] They differ somewhat from the values of ΔS_1° and ΔS_2° actually listed by this author.[36]

postulates of course that the covalent contribution to the bonding energy is large enough to be an important term in ΔH°. For typically hard-hard interactions, as are the formation reactions of the fluoride and sulphate complexes discussed here, this is presumably not the case. The value of ΔH° will for such reactions be determined almost exclusively by the balance between the energy required to effect the necessary dehydration of acceptor and donor, and the electrostatic energy gained on the formation of the complex. How this balance changes from donor to donor is not easy to foresee.

A very important question in this connexion is how extensively the acceptor and the donor are dehydrated when the complexes are formed. The donor may either enter the inner coordination sphere of the acceptor, or it may be linked *via* one, or possibly more, water molecules, acting as bridges, *i.e.* inner or outer sphere complexes may be formed. The energy balance will evidently be different for the two alternatives. The systems listed in Table 6 are certainly all inner sphere,[37] and the rule formulated above thus applies to complexes of this type. For outer sphere complexes, the experimental data available do not warrant any conclusions about the relative magnitude of ΔH_j° for fluoride and sulphate complexes.

REFERENCES

1. Ahrland, S. and Kullberg, L. *Acta Chem. Scand.* **25** (1971) 3457.
2. Ahrland, S. and Kullberg, L. *Acta Chem. Scand.* **25** (1971) 3471.
3. Ahrland, S. and Kullberg, L. *Acta Chem. Scand.* **25** (1971) 3677.
4. Ahrland, S. *Struct. Bonding* **5** (1968) 118.
5. Gerding, P. and Johansson, B. *Acta Chem. Scand.* **22** (1968) 2255.
6. Mironov, V. E., Kulba, F. Ya., Rutkovskii, Yu. I. and Ignatenko, E. I. *Zh. Neorg. Khim.* **11** (1966) 1786.
7. Saraiya, S. C. and Sundaram, A. K. *Proc. Symp. Electrode Processes* 1966, p. 50, as quoted in *Chem. Abstr.* **70** (1969) 314.
8. Frank, R. E. and Hume, D. N. *J. Am. Chem. Soc.* **75** (1953) 1736.
9. Fronæus, S. and Larsson, R. *Acta Chem. Scand.* **16** (1962) 1433.
10. Tribalat, S. and Dutheil, C. *Bull. Soc. Chim. France* **1960** (1) 160.
11. Fronæus, S. In Jonassen, H. B. and Weissberger, A. *Technique of Inorg. Chem.* Interscience, New York, London 1963, Vol. 1, Chapt. 1.
12. Sillén, L. G. and Liljekvist, B. *Svensk Kem. Tidskr.* **56** (1944) 85.
13. Persson, H. *Acta Chem. Scand.* **24** (1970) 3739.
14. Nancollas, G. H. and Torrance, K. *Inorg. Chem.* **6** (1967) 1567.
15. Golub, A. M. and Ivanchenko, G. D. *Zh. Neorg. Khim.* **3** (1958) 333.
16. Ciavatta, L. and Grimaldi, M. *Inorganica Chimica Acta* **4** (1970) 312.
17. Nyman, C. J. and Alberts, G. S. *Anal. Chem.* **32** (1960) 207.
18. Tanaka, N., Ebata, K. and Murayama, T. *Bull. Chem. Soc. Japan* **35** (1962) 124.
19. Toropova, V. F. *Zh. Neorg. Khim.* **1** (1956) 243.
20. Ahrland, S,. Chatt, J., Davies, N. R. and Williams, A. A. *J. Chem. Soc.* **1958** 264.
21. Leden, I. *Potentiometrisk undersökning av några kadmiumsalters komplexitet,* (Diss.), Lund, 1943.
22. Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 159.
23. Ingri, N. and Sillén, L. G. *Acta Chem. Scand.* **16** (1962) 173.
24. Schorsch, G. *Bull. Soc. Chim. France* **1964** 1456.
25. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quantitative Inorganic Analysis,* 3rd Ed., Macmillan, New York 1964.
26. Hansen, M. *Constitution of Binary Alloys,* 2nd Ed., 1958, p. 846, as quoted in *Gmelin,* 8th Ed., Nr. **34** [A] Quecksilber, 1962, p. 1062.
27. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
28. Morgan, T. D. B., Stedman, G. and Whincup, P. A. E. *J. Chem. Soc.* **1965** 4813.
29. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 747.
30. Fronæus, S. and Larsson, R. *Acta Chem. Scand.* **16** (1962) 1447, and references therein.
31. Ahrland, S. *Helv. Chim. Acta* **50** (1967) 306.
32. Carvalho, R. G. de and Choppin, G. R. *J. Inorg. Nucl. Chem.* **29** (1967) 737.
33. Paul, A. D., Gallo, L. S. and Van Camp, J. B. *J. Phys. Chem.* **65** (1961) 441.
34. Izatt, R. M., Eatough, D., Christensen, J. J. and Bartholomew, C. H. *J. Chem. Soc.* **A 1969** 47.
35. Zielen, A. J. *J. Am. Chem. Soc.* **81** (1959) 5022.
36. Baumann, E. W. *J. Inorg. Nucl. Chem.* **32** (1970) 3823.
37. Ahrland, S. *Proc. 3rd Symp. Coord. Chem., Debrecen Hungary, 1970,* Akademiai Kiado, Budapest, vol. 1, p. 13, vol. 2, p. 167.