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Thermodynamics of Metal Complex Formation in Aqueous Solution. V. Equilibrium and Enthalpy Measurements on the Copper(II) and Nickel(II) Thiocyanate Systems

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The stability constants and the enthalpy changes for the formation of copper(II) and nickel(II) thiocyanate complexes in aqueous solution have been determined by means of a calorimetric titration method. For the copper(II) thiocyanate system the stability constants have also been determined spectrophotometrically. From the measured enthalpy changes, and the free energy changes computed from the stability constants, the entropy changes have been calculated. All data refer to 25.0 °C and an aqueous sodium perchlorate medium of ionic strength 1.00 M.

In the thiocyanate systems studied, all the species are formed in modestly exothermic reactions. The entropy terms are all negative.

In previous papers of this series [3,4] the changes of free energy, enthalpy, and entropy accompanying the formation of a number of thiocyanate complexes have been reported. Besides the uranyl(VI) ion the metals used have been the divalent ions of electron configuration d^{10}, *viz.* Zn^{2+}, Cd^{2+}, and Hg^{2+} of which Zn^{2+} is classified as a hard acceptor, Cd^{2+} as mildly soft and Hg^{2+} as a very soft one.[5]

It should also be of interest to study how the thermodynamic functions for the formation of thiocyanate vary along the long rows of the Periodic Table. In this work the complexes of copper(II) and nickel(II) have been studied, making it possible to compare the coordination of SCN^- to the three acceptors Zn^{2+}, Cu^{2+}, and Ni^{2+}, all on the borderline between hard and soft.[5]

Like the earlier investigations in this series,[1-4] 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 copper(II)

Table 1. Comparison of reported values of stability constants and enthalpy changes for the copper(II) and nickel(II) thiocyanate systems. The values given are the overall standard changes.

System		$Cu^{2+}-SCN^-$			$Ni^{2+}-SCN^-$							
Ref.		6	7	8	9	10	7	11	13	8	12	14
Temp./°C		25	25	25	20		25	25	20	25	25	25
I/M		0.5[a]	0.2	$I\rightarrow 0$	1.0[b]	varying	0.2	1.0[b]	1.5[b]	$I\rightarrow 0$	0.7[c]	$I\rightarrow 0$
β_j/M^{-j}	$j=1$	55.1	52.9	213	15.0	15.0	15.7	14.9	13.8	58	17.5	95
	2	347			44				56			
	3	490			65				50			
	4	970							100			
$-\Delta H°_1$/ kJ mol^{-1}				12.6						9.4	14.4	21.5

[a] KNO_3, [b] $NaClO_4$, [c] $HClO_4$

thiocyanate system have previously been determined spectrophotometrically,[6,7] Table 1. For the same system a value of ΔH°_1 at $I=0$ has been obtained from calorimetric measurements.[8]

Several experimental methods have been used in the study of nickel thiocyanate complexes, Table 1, *viz.* cation exchange,[9] spectrophotometry, [7,10] polarography,[11,12] extraction measurements,[13] and potentiometric measurements by means of a silver – silver thiocyanate electrode.[14] The enthalpy change, ΔH°_1, for the first step has been determined both calorimetrically [8] and from the temperature dependence of β_1.[12,14]

For weak or moderately strong complexes, $0<\log K<3$, a titration calorimeter may be a good tool to determine equilibrium constants as well as enthalpy changes provided the enthalpy changes are not too small.[3,15] It is evident from Table 1 that for both the copper(II) and nickel(II) systems β_j and ΔH_j are of the right magnitude to allow a calorimetric determination of these quantities. Such a determination has therefore been undertaken. In order to check the stability constants obtained a spectrophotometric study of the copper(II) thiocyanate has also been performed. From cation exchange and spectrophotometric measurements the stability constants of the nickel thiocyanate system have been determined by Fronæus [9] for the medium used in this study. These constants refer admittedly to 20 °C but they can be recalculated to 25 °C by an iterative procedure once preliminary values of ΔH_j have been found.[3]

CALCULATIONS

The notation is the same as in parts I and II of this series [1,2] with the following additions:

A = absorbance

l = sample path length

λ = wavelength

$a = A/l$

ε_M, ε_L, ε_j = the molar absorptivities of M, L, and the complex ML_j

$$\varepsilon = (a - \varepsilon_M C_M - \varepsilon_L C_L)/C_M \quad (1)$$

$\varepsilon^* = a/C_M$

Q_{exp} = heat change after addition of titrant (>0 if heat is evolved)

Q_{corr} = heat change corrected for heat of dilution

Calculation of stability constants from spectrophotometric measurements. One graphical and one numerical method of calculation have been used. The graphical method has been described previously.[16] Only its main points will therefore be given here.

Assuming that only mononuclear complexes are formed and that Beer's law can be applied to the complex solutions, we get

$$a = \varepsilon_M[M] + \varepsilon_L[L] + \sum_{j=1}^{N} \varepsilon_j[ML_j] \quad (2)$$

Introducing the stability constants we obtain from eqns. (1) and (2):

$$\varepsilon = \left[\sum_{j=1}^{N} (\varepsilon_j - \varepsilon_M - j\varepsilon_L)\beta_j[L]^j\right] \Big/ \left(1 + \sum_{j=1}^{N} \beta_j[L]^j\right) \quad (3)$$

From eqn. (3) it is evident that a constant value of ε implies a constant value of [L] and hence a constant ligand number $\bar{n}$, *cf.* Ref. 1. From the definition of $\bar{n}$

$$C_L = \bar{n}C_M + [L] \quad (4)$$

If ε is measured as a function of C_L for a number of different C_M, a family of curves is obtained where the same value of ε in the different curves means the same value of [L] and also of $\bar{n}$. Cutting the curves at a constant value of ε and plotting corresponding values of C_L and C_M should result, according to eqn. (4), in a straight line with the intercept on the C_L-axis = [L] and the slope = $\bar{n}$. Once corresponding values of $\bar{n}$ and [L] are known, the stability constants are graphically evaluated.[1]

For the numerical calculations the least-squares programme "Letagrop Spefo" developed by Sillén and Warnqvist [17] has been used. The input data were the total concentrations C_M and C_L and the molar absorptivity, ε^*, of each solution. The error square sum to be minimized was

$$U_{rel} = \sum_i (\varepsilon^*_{i,calc} - \varepsilon^*_{i,exp})^2 (\varepsilon^*_{i,exp})^{-2} \quad (5)$$

The calculation gives the stability constants, β_j, and the molar absorptivities of the absorbing species. The molar absorptivities of free ligand and free metal were determined separately (see "Measurements and results") and then regarded as known parameters during the calculations.

Calculation of enthalpy changes and stability constants from calorimetric measurements. Assuming only mononuclear complexes, ML_j, the total heat of reaction between M and L in solution is given by

$$Q_{calc} = -V \sum_{j=1}^{N} [ML_j] \Delta H_j \quad (6)$$

ΔH_j is the overall enthalpy of formation. Introduction of the expressions for the stability constants β_j in eqn. (6) yields

$$Q_{calc} = -V[M] \sum_{j=1}^{N} \beta_j [L]^j \Delta H_j \quad (7)$$

Knowing the total concentrations of metal, C_M, and ligand, C_L, the concentrations [M] and [L] can be calculated once the β_j-values are known. Thus Q_{calc} is a function of only β_j and ΔH_j.

By making a least-squares analysis of the error square sum equation

$$U(\beta_j, \Delta H_j) = \sum_{i=1}^{N} w_i (Q_{i,calc} - Q_{i,corr})^2 \quad (8)$$

where w_i is a weighting term and Q_{corr} the measured heat effects corrected for heats of dilution, a set of unknown parameters β_j and ΔH_j, which minimizes the error square sum U, can be found.

For the calculation of ΔH_j from eqn. (8) in cases where values of β_j are known the least-squares programme "Letagrop Kalle" [18] has previously been used.[2] This programme fails, however, if asked to produce simultaneously all the unknown parameters ΔH_j and β_j. Therefore we decided to construct a new least-squares programme called "Kalori" which could treat both the enthalpy changes and the equilibrium constants as unknown parameters simultaneously. For details of this programme, see Ref. 19.

EXPERIMENTAL

Chemicals. Nickel perchlorate was prepared by dissolving nickel carbonate (Merck's *p.a.*) in perchloric acid (Baker's Analyzed) and was recrystallized a few times from water. The nickel(II) concentration of the stock solution was determined by electrolysis in ammonical solution according to Okáč.[20] In order to avoid hydrolysis of nickel [21] a small excess (about 1/10 of the nickel(II) concentration) of perchloric acid was added to the stock solution. The concentration of free acid was determined potentiometrically.[22] *Copper(II) perchlorate* (G. F. Smith) was recrystallized three times from water. The stock solution was analyzed by electrodeposition. Also to this solution, excess acid (about 1/10 of the copper(II) concentration) was added in order to prevent hydrolysis.[23] *The sodium thiocyanate* (Baker's Analyzed) stock solution was standardized both by Volhard titration and gravimetrically (precipitation of AgSCN). *Sodium perchlorate* was prepared and analyzed as before.[1]

The spectrophotometric measurements were carried out mainly with a Zeiss PMQ II Spectrophotometer. Suitable wavelengths for the measurements were selected from absorption curves of copper(II) solutions with and without thiocyanate, recorded with a Hitachi recording spectrophotometer, Fig. 1. The thiocyanate curve, B, has a relative maximum at 348 nm, where the absorption differs considerably from that of the hydrated copper(II) ion, curve A. As the systematic error in the measured absorbance caused by imperfectly monochromatic light disappears where the curve has a horizontal tangent, this wavelength was selected. Curve B has another absorption peak at 800 nm, Fig. 1, but here also curve A shows high values of ε, which lowers the precision of the measurements undertaken at this wavelength. As measurements carried out at different absorption bands are likely to reveal the possible existence of polynuclear complexes,[16] some measurements have nevertheless been performed at 800 nm.

The solutions were made up in 50 cm³ measuring flasks from stock solutions of copper(II) perchlorate, sodium perchlorate, and sodium thiocyanate. The absorbance was meas-

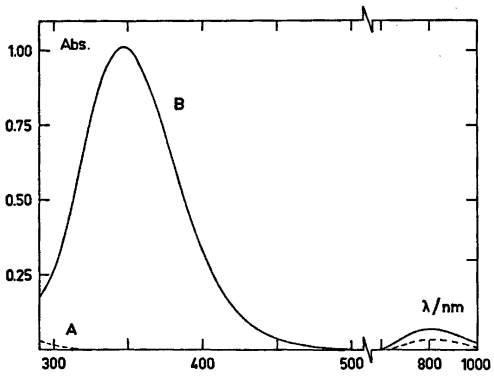

Fig. 1. Absorption curves of free copper(II) ions and a mixture of copper(II) and thiocyanate ions at 25 °C and at ionic strengths of 1.0 M and a cell thickness of 4.00 cm. A. 1.00 mM $Cu(ClO_4)_2$. B. 1.00 mM $Cu(ClO_4)_2$ + 16.00 mM NaSCN.

ured immediately after mixing, as copper(II) thiocyanate on standing disintegrates with the formation of slightly soluble copper(I) thiocyanate.[24]

In each series of measurements, C_M and the cell thickness l were kept constant. For each wavelength all series had a constant product lC_M, *viz.* 0.00200 and 0.0200 cm M for 348 and 800 nm, respectively. For each wavelength, solutions of the same value of ε are thus measured at the same total absorbance which eliminates several systematic errors in the determination of $\bar{n}$. These include errors due to reflections in the end-plates of the absorption cells, and also errors due to imperfect monochromaticity, inasmuch as these have not already been eliminated by selecting an absorption maximum for measurement.[16]

At $\lambda = 348$ nm, series have been carried out with $l = 0.1$, 0.2, 0.5, and 1.0 cm and at 800 nm with $l = 1.0$, 2.0, and 4.0 cm. As the true absorbances of the solutions are not essential, the absolute path lengths of the quartz cells used are not required but only the ratios between them. These ratios were determined by measurements on alkaline picrate solutions.[25] The thickness of the 1 cm cell was set equal to 1.000 cm.

All measurements were repeated at least three times. The solution to be measured and the cell compartment of the spectrophotometer were thermostated at 25.0 ± 0.1 °C.

Calorimetric measurements. The calorimeter and the technique of measurement have been described previously.[2] In each titration series, the reaction vessel initially contained V_0 cm³ of a solution S and a titrant T was then added. When the vessel had been almost filled solution was removed so that the initial volume V_0 was restored. The compositions of the solutions S and T are given in Tables 4 and 5. In order to determine the corrections for the heats of dilution, series analogous to those of the main measurements were performed except that only one of the two reactants was present.

Electrical calibration showed that the heat equivalent, ε_v, was a linear function of the total volume, V, according to

$$\varepsilon_v = 2.091 + 0.0226(V - 90.0)$$

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

MEASUREMENTS AND RESULTS

Spectrophotometric measurements on copper(II) thiocyanate. The experimental data are collected in Table 2. At high thiocyanate concentrations the disintegration of the copper(II) thiocyanate solutions mentioned above proceeds quite rapidly which makes the measurements difficult. The highest C_L-value yielding reasonably reproducible results was 80 mM.

Table 2. Experimental values of ε^*_{Cu} cm^{-1}M^{-1} at different values of C_L and C_M at 348 and 800 nm.

λ/nm	348				800		
C_M/mM	2	4	10	20	5	10	20
C_L/mM							
1	22.0	20.2	16.3	12.1	12.45	12.25	12.10
2	43.5	39.4	31.7	23.5	13.15	12.84	12.51
3	64.0	57.9	47.3	35.3	13.75	13.38	12.96
5	101.5	93.8	76.6	58.2	14.95	14.38	13.75
7	137.0	126.7	104.9	80.3	16.07	15.35	14.50
10	184.5	172.1	145.2	112.8	17.74	16.80	15.63
12	212.0	200.0	170.7	134.2	18.55	17.75	16.40
15	253.5	239.4	207.1	164.0	20.05	19.01	17.48
17	279.8	264.1	229.1	183.2	20.80	19.80	18.10
20	313.8	298.8	262.0	212.7	22.12	20.95	19.18
25	364.8	350.2	311.2	257.5	24.00	22.84	20.69
30	411.0	396.0	356.5	299.2	25.75	24.51	22.34
35	451.5	436.2	398.1	339.2	27.20	26.04	23.74
40	489.3	474.9	437.2	375.2	28.70	27.77	25.19
45	522.3	508.3	472.5	410.0	30.00	29.19	–
50	553.0	540.2	505.2	441.4	31.15	30.29	27.74
55	580.0	567.6	534.4	470.9	–	–	–
60	605.5	595.3	562.1	500.2	33.45	32.45	30.38
70	650.5	641.0	610.6	–	35.65	34.39	–
80	689.0	682.4	653.1	–	–	–	–

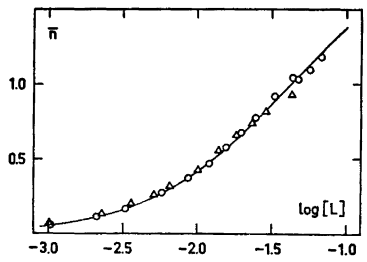

Fig. 2. The complex formation function of the copper(II)thiocyanate system. The fulldrawn curve has been computed from eqn. (4) of Ref. 4 using $\beta_1 = 55$ M^{-1} and $\beta_2 = 550$ M^{-2}. The values of $\bar{n}$ obtained from the slopes of the (C_M, C_L)-lines are denoted by (○), for $\lambda = 348$ nm, and (△), for $\lambda = 800$ nm. [(L) in M].

The molar absorptivities for the copper(II) ion, ε_{Cu}, and the thiocyanate ion, ε_L, were determined separately. The value of ε_{Cu} was considerable ($= 11.70$ cm^{-1} M^{-1}) at 800 nm but negligible at 348 nm. The value of ε_L was low at both wavelengths (0.007 cm^{-1} M^{-1} at 348 nm; < 0.001 cm^{-1} M^{-1} at 800 nm).

From the graphical evaluation the stability constants of the first two complexes were found, Table 3. In the range investigated ($C_L < 80$ mM) there was no sign of a third complex. Values of $\bar{n}$ obtained from the slopes of (C_M, C_L)-lines have been plotted in Fig. 2.

The results of the computer calculations with the least-squares programme "Letagrop Spefo" are also given in Table 3. The experiments are well described by a model including two complexes but as seen from the error square sum, U, a somewhat better fit results for the data at 348 nm if a third complex is introduced. The values of σ, the standard deviation for the relative differences between experimental and calculated values of ε^*, are quite small, Table 3. Due to the high absorption of Cu^{2+} at 800 nm the results derived from the measurements at this wavelength are not very precise. This is indicated by the relatively large standard deviations in the β_j-values. In view of this the agreement between the two sets of β_j obtained at 348 nm and 800 nm is quite satisfactory, Table 3.

Calorimetric measurements on copper(II) thiocyanate. The experimental data are collected in Table 4. The value of C_M varied from 5 to 20 mM. As these measurements were more time-consuming than the spectrophotometric ones the highest value of C_L which could be reached without a significant decomposition of copper(II) thiocyanate was only 60 mM. The spectrophotometric measurements show that only two complexes exist in the concentration range studied and that the second one never exceeds $\simeq 25$ % of the total. The complex formation is moreover fairly weak. A determination of the stability constants from calorimetric data should thus be feasible.

Using the computer programme "Letagrop Kalle" the error square sum, U, was calculated for different sets of β_1 and β_2. Starting with

Table 3. Stability constants for the copper(II) thiocyanate system obtained from spectrophotometric and calorimetric measurements. The errors given correspond to three standard deviations given by the computer or to estimated errors.

Method	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}	U	σ
Spectr. at $\lambda = 348$ nm					
Letagrop	55.9 ± 0.9	500 ± 30		0.00223	0.0055
Letagrop	54.6 ± 1.2	580 ± 60	640 ± 70	0.00137	0.0043
Graphically	55.0 ± 0.5	600 ± 50			
Spectr. at $\lambda = 800$ nm					
Letagrop	67 ± 7	420 ± 100		0.00070	0.0038
Graphically	65 ± 8	460 ± 150			
Calorimetrically					
Kalori	53.4 ± 6.3	520 ± 90		0.00506	0.020
Graphically	53.5 ± 4	520 ± 60			
'Best' values	55 ± 2	550 ± 50			

Table 4. Determination of the heats of formation for the copper(II) thiocyanate complexes.[a] For all the series: $V_0 = 100.0$ cm³ and $V = (V_0 + v)$ cm³.

(a) ○ S: $C_M = 0.02000$ M, $C_{NaClO_4} = 0.940$ M. T: $C_L = 0.500$ M, $C_{NaClO_4} = 0.500$ M.
v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 2.000, 5.995, 6.059, 0.001; 4.000, 4.973, 5.038, −0.021; 6.000, 4.070, 4.136, −0.008; 8.000, 3.280, 3.347, 0.052;

(b) □ S: $C_M = 0.01000$ M, $C_{NaClO_4} = 0.970$ M. T: $C_L = 0.500$ M, $C_{NaClO_4} = 0.500$ M.
v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 2.000, 3.803, 3.867, −0.012; 4.000, 2.804, 2.869, −0.014; 6.000, 2.117, 2.183, −0.019; 8.000, 1.629, 1.696, −0.013;

(c) △ S: $C_M = 0.005000$ M, $C_{NaClO_4} = 0.985$ M. T: $C_L = 0.500$ M, $C_{NaClO_4} = 0.500$ M.
v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 2.000, 2.152, 2.216, −0.003; 4.000, 1.439, 1.504, −0.004; 6.000, 1.011, 1.077, 0.005; 8.000, 0.752, 0.819, −0.001;

(d) ▽ S: $C_M = 0.005000$ M, $C_{NaClO_4} = 0.985$ M. T: $C_L = 1.000$ M.
v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 4.479, 4.846, 0.022; 6.000, 1.722, 2.073, −0.013;

(e) ◇ S: $C_M = 0.005000$ M, $C_{NaClO_4} = 0.985$ M. T: $C_L = 1.000$ M.
v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 2.000, 3.489, 3.734, 0.022; 5.000, 2.296, 2.649, −0.019;

[a] The values of ΔQ_{corr} refer to the deviations ($Q_{calc} - Q_{corr}$) obtained using the 'best' set of constants, *i.e.* $\beta_1 = 55$ M^{-1} and $\beta_2 = 550$ M^{-2}.

the set of constants found spectrophotometrically, new combinations of β_1 and β_2 were systematically tried. The dependence of $U(\beta_j, \Delta H_j)$ on the values of β_1 and β_2 chosen is summarized in Fig. 3. The two constants giving the minimum of the error square sum according to the graph are given in Table 3.

An analysis of the calorimetric data was also made using the new computer programme "Kalori" which could treat both β_j and ΔH_j as unknown parameters simultaneously. The β_1 and β_2 values obtained by the computer are collected in Table 3, from which it can be seen that the two evaluation methods applied on the calorimetric data give identical β_j-values. This shows that the new programme "Kalori" works well.

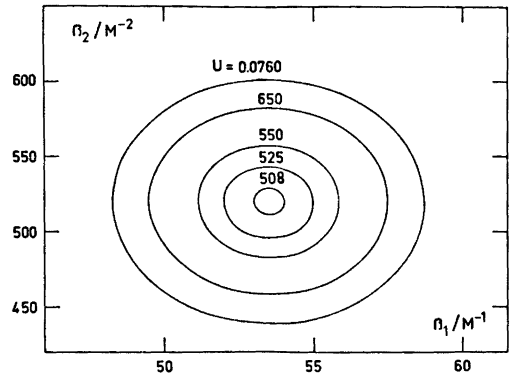

Fig. 3. Plot of assumed values of U *vs.* β_1 and β_2 for the copper(II) thiocyanate system.

It is also evident from Table 3 that the spectrophotometric (at 348 nm) and the calorimetric measurements give very consistent β_j-values. The set of constants considered to be the 'best' one is listed in Table 7. Using these constants, values of $\Delta G°_j$, $\Delta H°_j$ and $\Delta S°_j$ have been calculated and are collected in Table 7. In Fig. 4 the Δh_v-function is plotted *versus* $\bar{n}$, calculated from the 'best' values of β_j (see above). The Δh_v-function is independent of C_M, which proves that no polynuclear complexes exist. The fulldrawn curve is calculated from the stability constants and enthalpy changes listed in Table 7.

Calorimetric measurements on nickel(II) thiocyanate. Seven titration series have been carried out, Table 5. In three of these, a−c, ligand was added to a solution of the metal ion. In order to reach higher values of [L] and hence of $\bar{n}$, four series, d−g, have been performed by adding a metal solution to ligand solutions. As mentioned on p. 831 the nickel

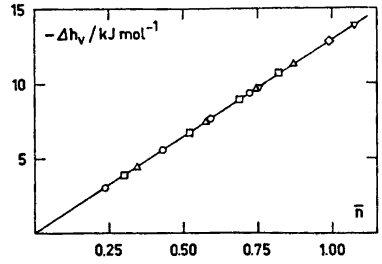

Fig. 4. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the copper(II)-thiocyanate system, *cf.* Table 4.

Table 5. Determination of the heats of formation for the nickel thiocyanate complexes.[a] For all the series: $V_0 = 90.00$ cm³ and $V = (V_0 + v)$ cm³.

(a) ○ S: $C_M = 0.05000$ M, $C_{NaClO_4} = 0.850$ M. T: $C_L = 1.000$ M

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 12.605, 12.950, −0.020; 6.000, 9.732, 10.066, 0.055; 9.000, 7.704, 8.025, 0.022; 12.000, 6.231, 6.543, −0.022; 15.000, 5.082, 5.383, 0.002; 18.000, 4.240, 4.532, −0.008; 21.000, 3.594, 3.876, −0.017; 24.000, 3.054, 3.325, 0.010; 27.000, 2.659, 2.921, −0.007;

(b) ○ S: $C_M = 0.03846$ M, $C_L = 0.2308$ M, $C_{NaClO_4} = 0.654$ M. T: $C_L = 1.000$ M.

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 2.327, 2.539, −0.013; 6.000, 1.934, 2.132, 0.047; 9.000, 1.676, 1.864, 0.037; 12.000, 1.461, 1.638, 0.037; 15.000, 1.294, 1.464, 0.025; 18.000, 1.149, 1.314, 0.020;

(c) □ S: $C_M = 0.03000$ M, $C_{NaClO_4} = 0.910$ M. T: $C_L = 1.000$ M.

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 8.555, 8.900, −0.016; 6.000, 6.131, 6.465, 0.056; 9.000, 4.675, 4.996, −0.026; 12.000, 3.626, 3.938, −0.020; 15.000, 2.903, 3.204, −0.025; 18.000, 2.363, 2.655, −0.016; 21.000, 1.968, 2.250, −0.017; 24.000, 1.651, 1.922, −0.002; 27.000, 1.438, 1.700, −0.028;

(d) □ S: $C_M = 0.02308$ M, $C_L = 0.2308$ M, $C_{NaClO_4} = 0.700$ M. T: $C_L = 1.000$ M.

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 1.214, 1.426, 0.020; 6.000, 1.049, 1.247, −0.003; 9.000, 0.891, 1.079, 0.005; 12.000, 0.748, 0.925, 0.029; 15.000, 0.662, 0.832, 0.016; 18.000, 0.595, 0.760, −0.001;

(e) △ S: $C_M = 0.01500$ M, $C_{NaClO_4} = 0.955$ M. T: $C_L = 1.000$ M.

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 4.655, 5.000, −0.036; 6.000, 3.073, 3.407, 0.010; 9.000, 2.198, 2.519, −0.006; 12.000, 1.637, 1.949, −0.008; 15.000, 1.276, 1.577, −0.022; 18.000, 1.014, 1.306, −0.024; 21.000, 0.799, 1.081, −0.001; 24.000, 0.689, 0.960, −0.035; 27.000, 0.548, 0.810, −0.006;

(f) △ S: $C_M = 0.01154$ M, $C_L = 0.2308$ M, $C_{NaClO_4} = 0.735$ M. T: $C_L = 1.000$ M.

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 0.502, 0.714, −0.020; 6.000, 0.411, 0.609, −0.012; 9.000, 0.333, 0.521, −0.001; 12.000, 0.274, 0.451, 0.007; 15.000, 0.219, 0.389, 0.018; 18.000, 0.199, 0.364, 0.000;

(g) ▼ S: $C_L = 0.4000$ 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, ΔQ_{corr}/J: 3.000, 4.934, 5.143, 0.039; 6.000, 4.767, 4.974, 0.038; 9.000, 4.618, 4.822, 0.027;

(h) ▲ S: $C_L = 0.5000$, $C_{NaClO_4} = 0.500$ M. T: $C_M = 0.1000$, $C_{NaClO_4} = 0.700$ M.

v/cm³, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: 3.000, 5.375, 5.617, −0.001; 6.000, 5.230, 5.471, −0.019; 9.000, 5.084, 5.323, −0.029;

(i) ■ S: $C_L = 0.6000$ 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, ΔQ_{corr}/J: 3.000, 5.687, 5.970, 0.003; 6.000, 5.534, 5.817, −0.005; 9.000, 5.384, 5.666, −0.007;

(j) ● S: $C_L = 0.8000$ 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, ΔQ_{corr}/J: 3.000, 6.123, 6.512, 0.020; 6.000, 6.036, 6.399, −0.020; 9.000, 5.928, 6.284, −0.051;

[a] The values of ΔQ_{corr} refer to the deviations $(Q_{calc} - Q_{corr})$ for the set of constants giving the minimum of the error square sum.

solutions contained perchloric acid in order to avoid hydrolysis.

From spectrophotometric and cation exchange measurements Fronæus [9] found three complexes for this system. The stability constants determined at 20.0 °C have been recalculated to 25.0 °C by an iterative method.[3] The values of β_j valid at 25.0 °C are given in Table 6.

A determination of the stability constants from the calorimetric data has been performed. As there are evidently three complexes in this system a determination of the β_j-values by the 'schematic map' method is a little more complicated in this case. However, starting with the set of constants found by Fronæus the error square sum, U, was calculated for a number of different sets of β_2 and β_3 (β_1 was kept constant). From the plot of $U(\beta_j, \Delta H_j)$ *versus* β_2 and β_3 the values of these two parameters giving the minimum of the error square sum was found. In the next approximation $\beta_3 (= 18\ M^{-3})$ was kept constant while $U(\beta_j, \Delta H_j)$ was calculated for various values of β_1 and β_2, see Fig. 5. The graphically obtained set of constants giving the minimum of the error square sum is given in Table 6. In the same

Table 6. Stability constants for the nickel(II) thiocyanate system obtained from calorimetric and cation exchange measurements. The errors given correspond to three standard deviations given by the computer or to estimated errors.

Method	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}
Calorimetrically			
Kalori	13.3 ± 1.2	37 ± 10	19 ± 18
Graphically	13.4 ± 0.7	37 ± 5	18 ± 12
By cation exchange [a]	13.8 ± 0.5	38 ± 4	54 ± 10
'Best' values	13.8 ± 0.5	38 ± 4	40 ± 15

[a] Values taken from Ref. 9, recalculated to 25.0 °C.

Table the stability constants computed by the programme "Kalori" are also included. The standard deviation, σQ_{corr}, was found to be equal to 0.024 J. As seen, the two calculation methods give almost identical results, once more indicating that the programme "Kalori" works properly.

The stability constants of the nickel(II) thiocyanate system obtained from calorimetric measurements are quite in line with those found by ion exchange, Table 6. The two methods give practically the same values of β_1 and β_2, respectively, while the value of β_3 determined in this study is lower than that found before. It is difficult to find a good value of β_3 by any method as the third complex is very weak ($K_3 = \beta_3/\beta_2 \approx 1$). The values of β_j obtained calorimetrically have somewhat higher random errors than those found by the cation exchange method. The set of 'best' values of β_j has been selected with due consideration to this, Table 6. These constants have then been used for the calculation of $\Delta H°_j$. The standard deviation, σQ_{corr}, was found to be equal to 0.035 J. In Fig. 6, Δh_v is plotted *versus* $\bar{n}$ (calculated from the 'best' constants). No variation of Δh_v with C_M can be discerned. Consequently no polynuclear complexes are formed. The β_j-values used, together with corresponding values of $\Delta G°_j$, $\Delta H°_j$ and $\Delta S°_j$, are listed in Table 7.

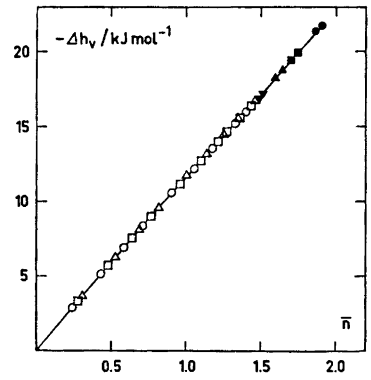

Fig. 6. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the nickel(II)-thiocyanate system; *cf.* Table 5.

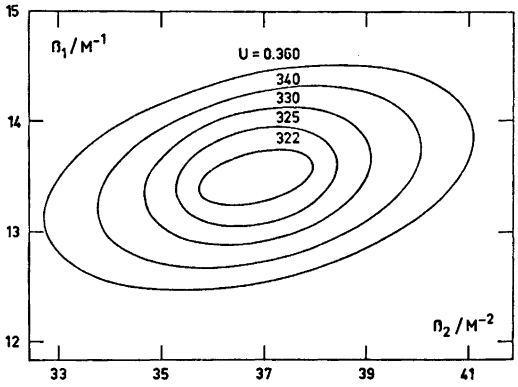

Fig. 5. Plot of assumed values of U *vs.* β_1 and β_2 for the nickel(II) thiocyanate system. $\beta_3 = 18\ M^{-3}$.

DISCUSSION AND CONCLUSIONS

For the copper(II) thiocyanate system our value of β_1 (55 M^{-1}) agrees very well with those

Table 7. The stability constants used and the computed values of $\Delta G°_j$, $\Delta H°_j$ and $\Delta S°_j$ for the stepwise reactions of the nickel, copper(II) and zinc thiocyanate systems. The data for the zinc system are taken from Ref. 4. The errors given correspond to three standard deviations or to estimated errors.

Metal		Ni^{2+}	Cu^{2+}	Zn^{2+}
β_j/M^{-j}	$j=1$	13.8 ±0.5	55 ±2	5.10 ±0.03
	2	38 ±4	550 ±50	11.0 ±0.6
	3	40 ±15		15.0 ±3.6
	4			32 ±5
$-\Delta G°_j/$ kJ mol^{-1}	1	6.51 ±0.10	9.93 ±0.09	4.04 ±0.02
	2	2.51 ±0.30	5.71 ±0.25	1.91 ±0.14
	3	0.1 ±0.9		0.76 ±0.6
	4			1.87 ±0.8
$-\Delta H°_j/$ kJ mol^{-1}	1	12.02 ±0.15	12.65 ±0.20	5.80 ±0.15
	2	8.9 ±1.0	13.1 ±1.5	1.8 ±1.0
	3	8.2 ±4.0		0.8 ±3.0
	4			7.7 ±3.5
$\Delta S°_j/$ J mol^{-1} K^{-1}	1	−18.5 ±0.6	−9.1 ±0.7	−5.9 ±0.5
	2	−21.5 ±3.5	−25 ±5	0 ±4
	3	−27 ±13		0 ±10
	4			−19 ±12

reported by Tanaka and Takamura [6] and by Kodama and Hanawa,[7] see Table 1. The value of β_2 given in Ref. 6, on the other hand, is lower than ours which may be due to the difference in ionic medium.

For the nickel(II) thiocyanate system our calorimetrically determined β_j-values agree very well with those reported by Fronæus, as already mentioned. On the whole they are also compatible with the set of constants found by Tribalat and Caldero, Table 1.

Nancollas and Torrance [8] have calorimetrically determined $\Delta H°_1$ for the formation of thiocyanate complexes of some transition metals at $I=0$. As previously pointed out,[4] their values for the cadmium and zinc thiocyanate systems are considerably less exothermic than those found by Gerding and Johansson [26] and by us. Similarly, for the nickel(II) thiocyanate system our value of $\Delta H°_1$, −12.02 kJ mol^{-1}, is more negative than that found by Nancollas and Torrance, −9.4 kJ mol^{-1}. For the copper(II) thiocyanate system, however, their value of $\Delta H°_1$, −12.6 kJ mol^{-1}, is consistent with ours, −12.65 kJ mol^{-1}. The discrepancies between the values given by Nancollas and Torrance and those obtained at $I=1.0$ M can hardly be due only to the difference in ionic medium.

A more likely explanation is no doubt that for these fairly weak complexes the introduction of even modestly erroneous values of β_j results in relatively large errors in the calculated amounts of the various complexes formed in a given solution. As, for a certain complex, the measured heat change is the product of the amout of the complex formed and the enthalpy change of the complex formation, $\Delta H°_j$, a corresponding error will be introduced in $\Delta H°_j$. For their determinations, Nancollas and Torrance recalculated thermodynamic constants K_1 taken from various sources to the actual ionic strengths ($I<0.06$ M) of their experiments by means of a Debye-Hückel formula. This approach is no doubt likely to introduce errors and inconsistencies serious enough to impair the validity of a comparison between the various systems investigated. The method adopted here, *viz.* to determine the values of K together with the heat changes, or at least determination of the two quantities under identical conditions, should be preferable. Especially the values of K_1 chosen by Nancollas and Torrance for the zinc and cadmium thiocyanate systems, 71.4 M^{-1} and 322 M^{-2}, respectively, seem to be too high, *cf.* Ref. 14. Their values of $\Delta H°_1$ also differ most from ours in these two instances.

From the variation of β_1 with the temperature Das *et al.*[14] and Malyavinskaya and Turyan [12] have determined $\Delta H°_1$ of the nickel(II) thiocyanate system. The value reported by Das *et al.* is considerably more exothermic than ours while that of the latter investigators agrees fairly well, *cf.* Tables 1 and 7.

The three divalent first row transition metal ions Ni^{2+}, Cu^{2+}, and Zn^{2+} all generally behave as mildly hard acceptors with Cu^{2+} closest to the borderline between hard and soft.[5] It is then to be expected that the thiocyanate complexes of Cu^{2+} should be formed in more exothermic reactions than those of Ni^{2+} and Zn^{2+}. As seen from Table 7, this is the case. The difference between Cu^{2+} and Ni^{2+} is perhaps smaller than expected, however. Also the thiocyanate complexes of Cd^{2+}, considered to be an acceptor just on the soft side of the borderline, are in fact formed in less exothermic reactions than those of Ni^{2+}, Table 5 of Ref. 4.

The entropy changes are small and negative. As may be expected,[27] the values become on the whole more negative for each consecutive step.

The thiocyanate ion exhibits linkage isomerism, bonding to the metal ion either through its sulfur or nitrogen atom. Soft acceptors prefer the softer S and hard acceptors prefer the harder N. The metals of this study Ni^{2+}, Cu^{2+}, and Zn^{2+} are probably all N-bonded.[27,28]

Further discussion will be postponed until the complete results of this investigation have been reported.

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