

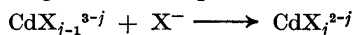
Thermochemical Studies on Metal Complexes

II. Free Energy, Enthalpy, and Entropy Changes for Stepwise Formation of Cadmium(II) Pseudo Halide Complexes in Aqueous Solution at 25°C*

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The enthalpy changes for the stepwise reactions:



where X^- is the cyanide, azide, thiocyanate, and nitrite ion, have been determined by a direct calorimetric titration procedure.

From these enthalpy changes and the changes in free energy, computed from known stability constants, the entropy changes have been calculated by the relation:

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

All data refer to an aqueous sodium perchlorate medium of ionic strength 3.00 M and a temperature of 25.00°C.

The variations with j of the free energy, enthalpy, and entropy changes, respectively, are similar for the four systems. The high stability of the cyanide system depends upon the enthalpy term, while the entropy term is of the same magnitude for all the four systems, and in all instances is it relatively unimportant to the complex formation.

The determination of the enthalpy changes of reactions has already been contributory towards a better understanding of the pattern of modern complex chemistry.¹ However, more data are necessary. This paper is part of a study concerned with determining the thermodynamic properties, ΔG° , ΔH° , and ΔS° , for the formation of a number of metal complexes in order to see how the stability of the complexes depends upon the enthalpy and entropy terms. The free energy change, ΔG_j° , is found from the relation:

$$\Delta G_j^\circ = -RT \ln K_j^\circ \quad (1)$$

* This work was first reported at the 12th. Northern Chemistry Conference in Trondheim Norway, June 16th. - 20th. 1965, and is abstracted in *Tidskrift for Kjemi, Bergvesen og Metallurgi*, No. 8-9, 1965.

and, when the enthalpy change, ΔH_j° , is determined, the entropy change, ΔS_j° , could be calculated from:

$$\Delta G_j^\circ = \Delta H_j^\circ - T\Delta S_j^\circ \quad (2)$$

Relation (2) also gives the complex stabilizing term. Earlier, the four cadmium(II) halide complex systems have been investigated,² and to obtain a comparison with other, more complicated, ligands, the study has been expanded to include the cadmium(II) cyanide, azide, thiocyanate, and nitrite systems.

The enthalpy changes of these systems have not previously been studied and compared systematically, and, furthermore, there exist very few papers employing calorimetric approach to these or similar systems. Golub *et al.* have given enthalpy values for the formation of $\text{Zn}(\text{SCN})_4^{2-}$ and of $\text{Cd}(\text{SCN})_2$ and $\text{Cd}(\text{SCN})_3^-$, determined from measurements of the stability constants at different temperatures^{3,4} (see Table 1). Tanaka *et al.* have studied the mercury thiocyanate system in the same way.⁵ Some metal cyanide systems have been studied by Christensen *et al.*,⁶⁻⁸ and for these the major factor contributing to the stability is the ΔH term, whilst the ΔS term is of little importance. From Table 1 it is seen that the zinc cyanide system is that most similar to the cadmium one. For the azide and the nitrite ions, no enthalpy investigations of systems having a central ion similar to cadmium(II) could be found.

The stability constants used in this work are taken from the literature⁹ — primarily those of Leden¹⁰ — except for the thiocyanate system where the

Table 1. Comparison of reported values of thermodynamic properties of some metal pseudo halide systems. The values given are the overall standard changes. Method to determine the enthalpy change: var. = from equilibrium measurements at different temperatures; cal. = from calorimetric measurements at direct titrations.

System	Zn—SCN	Cd—SCN	Hg—SCN	Ni—CN	Zn—CN	Hg—CN
Ref.	3	4	5	6	7	8
Method	var.	var.	var.	cal.	cal.	cal.
$-\sum_{k=1}^j \Delta G_k^\circ \times 10^{-3}$ (cal.mole ⁻¹)	$j=1$ 2 3 4	3.01 3.22	23.6 27.2 29.6		15.10 21.90 26.77	23.2 44.7 49.6 53.2
$-\sum_{k=1}^j \Delta H_k^\circ \times 10^{-3}$ (cal.mole ⁻¹)	1 2 3 4	4.2 6 5.7	30 29 36		10.8 19.2 27.8	23.0 48.5 56.1 63.3
$\sum_{k=1}^j \Delta S_k^\circ$ (cal.mole ⁻¹ degree ⁻¹)	1 2 3 4	-4 -9	-20 -6 -20		14.3 9.0 -3.3	0.7 -12.7 -21.7 -33.8

constants were redetermined by a potentiometric method.¹¹ From the known constants, the concentrations of the various complex species in the solutions and the changes in free energy have been computed. The calorimetric determinations of the various reaction heats were made using a reaction calorimeter and a titration procedure described previously.¹² The measurements were carried out at a temperature of 25.00°C, and in an aqueous sodium perchlorate medium of ionic strength 3.00 M. The hydrolysis of cadmium(II) was suppressed by a slight excess of perchloric acid (pH \approx 4).¹³

The calculations of the enthalpy values from the titration data and a list of symbols and equations used were described in a previous paper.² Two methods were tried: one graphical and one least squares method. The latter was developed by Sillén *et al.*^{14,15} and uses a high speed computer.

EXPERIMENTAL

Chemicals

If not otherwise stated, all chemicals were of analytical grade and were used without further purification.

Cadmium perchlorate was prepared by dissolving cadmium carbonate (Merck, *p. a.*) in an excess of perchloric acid (Baker Analyzed, *p. a.*). A 3 M stock solution was prepared, and from this the solutions used were made and analyzed by titration with EDTA (Merck, *p. a.*) using Erio-T as indicator. The solutions contained perchloric acid sufficient to maintain the pH at 4–5 to avoid hydrolysis of the cadmium(II) ion.¹³

Sodium perchlorate was prepared by neutralizing perchloric acid (Baker Analyzed, *p. a.*) with sodium carbonate (Merck, *p. a.*). For further details see Ref. 2. Tests showed no chloride or chlorate. Titration with acid gave a total concentration of weak protolytes to be less than 0.2 mM in a 3 M NaClO₄ solution. This impurity was neglected.

The ligand solutions of sodium cyanide, azide, thiocyanate, and nitrite were prepared from the salts (Baker Analyzed or Merck, *p. a.*) by weighing. The solutions were analyzed by titrations with silver nitrate or, for the nitrite system, with permanganate. The cyanide solution contained 0.200 M NaCN with 2.80 M NaClO₄ as ionic medium, and the hydrolysis of the cyanide ion was neglected. The azide solution was buffered with perchloric acid to 2.900 M NaN₃, 0.100 M HN₃, and NaClO₄ was added to obtain the required ionic strength of 3.00 M. The thiocyanate and the nitrite solutions were both 3.00 M with respect to ligand.

Procedure

The calorimeter and the titration procedure were the same as described in a previous paper.¹² This calorimeter was equipped with a device for the successive addition of known amounts of a titrant, and the measurements were performed by a series of titrations into a calorimeter solution, S, of 1–5 ml portions, up to a total of 25 ml, of a titration solution, T. The compositions of the solutions S and T were:

$$S \quad \left\{ \begin{array}{l} C_{Cd} \\ (3.000 - 3 C_{Cd}) \end{array} \right. \quad \left\{ \begin{array}{l} M \text{ Cd}(\text{ClO}_4)_2 \\ M \text{ NaClO}_4 \end{array} \right. \quad T \quad \left\{ \begin{array}{l} C_X \\ (3.000 - C_X) \end{array} \right. \quad \left\{ \begin{array}{l} M \text{ NaX} \\ M \text{ NaClO}_4 \end{array} \right.$$

$$X = \text{CN}, \text{N}_3, \text{SCN}, \text{or NO}_2$$

or, for some measurements of the cyanide system:

$$S \quad \left\{ \begin{array}{l} C_{CN} \\ (3.000 - C_{CN}) \end{array} \right. \quad \left\{ \begin{array}{l} M \text{ NaCN} \\ M \text{ NaClO}_4 \end{array} \right. \quad T \quad \left\{ \begin{array}{l} C_{Cd} \\ (3.000 - 3 C_{Cd}) \end{array} \right. \quad \left\{ \begin{array}{l} M \text{ Cd}(\text{ClO}_4)_2 \\ M \text{ NaClO}_4 \end{array} \right.$$

At least two series were carried out with the same pair of solutions.

The dilution heats of the ligands were determined by similar titration series, performed with no cadmium perchlorate in the solutions. For the central ion, however, no effect was found upon diluting from $C_{\text{Cd}} = 0.060$ to $C_{\text{Cd}} \approx 0.001$ in 3 M NaClO₄, and it was assumed that the dilution heats of the various complexes could also be neglected.

The thermodynamic standard state for the solute species M, A, and MA_j, where M is the central ion and A the ligand, in this study is a hypothetically ideal one molar solution having neutral salt to ionic strength 3.00 M. The zero superscript when used with ΔG , ΔH , and ΔS refers to the standard changes in these quantities with reference to this standard state.

MEASUREMENTS AND RESULTS

The electrical calibrations^{2,12} gave a linear dependence of the heat equivalent upon the total amount of titrant added, the closest fit being obtained by use of the method of least squares, giving the relationship:

$$-\varepsilon_v = 2.075 + 0.0194v \quad (3)$$

This function is valid for all the systems investigated here. The accuracy is better than 5×10^{-3} cal.ohm⁻¹ in the range $0 < v < 25$.

The cadmium(II) cyanide system. According to literature,^{10,16} the cyanide ion forms four mononuclear complexes with the cadmium ion, and these complexes are so strong that they are formed almost quantitatively in the

Table 2. The reaction and dilution heats for titration of the CN⁻ system at ionic strength 3.00 M. A solution, first with 0.050 M Cd²⁺ then without, is added into initially 100.0 ml 0.050 M CN⁻.

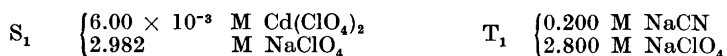
<i>v</i> (ml)	Cd ²⁺ (mmole)	Q _x (cal)	Q _{dil.} (cal)	Q _{corr.} (cal)	ΣQ _{corr.} (cal)	Δ <i>h_v</i> cal.mole ⁻¹
2.009	0.1005	2.946	-0.006	2.952	2.952	29 370
4.018	0.2009	2.942	0.000	2.948	5.900	29 370
6.027	0.3014	2.927	-0.011	2.933	8.833	29 300

Table 3. The dilution heats for 2.009 ml of the ligand solutions T added to a homogeneous mixture of 100.0 ml 3 M NaClO₄ and *v* - 2.0 ml of T.

<i>v</i> (ml)	Q _{dil.} (cal)							
	CN ⁻		N ₃ ⁻		SCN ⁻		NO ₂ ⁻	
2.009	0.072	0.075	0.833	0.856	-0.499	-0.505	0.123	0.133
4.018	0.000	0.020	0.777	0.796	-0.476	-0.491	0.123	0.133
6.027	0.009	0.013	0.773	0.749	-0.475	-0.464	0.136	0.131
8.036	-0.002	0.009	0.753	0.744	-0.435	-0.441	0.120	0.120
10.045	0.011	0.006	0.658	0.674	-0.435	-0.433	0.125	0.107
12.054	-0.002		0.676	0.687	-0.413	-0.427	0.108	0.129
14.063	0.007		0.650	0.666	-0.399	-0.401	0.120	0.155
16.072	0.005		0.621	0.637	-0.367	-0.374	0.112	0.129
18.081	0.010		0.609	0.615	-0.356	-0.363	0.108	0.115

range of concentrations used. Both sets of constants referred to were determined without any account being taken of the hydrolysis that occurred. Despite the rather large difference between the two sets, the enthalpy values calculated using them are nearly the same.

To avoid precipitation of $\text{Cd}(\text{CN})_2$ or $\text{Cd}(\text{OH})_2$ the total concentration of cadmium must be low, and for this reason the following compositions of the calorimeter solution S and the titration solution T were chosen:



To avoid association and neutralisation heats, the pH in the cadmium solution was adjusted to 5–6, which is possible without hydrolysis at this Cd^{2+} concentration.¹³ No corrections were made for the dilution of the central ion and the complex species or the heat effects from the hydrolysed cyanide. All are negligible. The heats of mixing were measured by titrations of T_1 into 3.000 M NaClO_4 and with the exception of the first addition, where a slight effect of neutralisation was noticed, no dilution heats of the ligand could be found. Corresponding values of v and Q_{dil} are given in Table 3, and of v and $\sum Q_{\text{corr}}$ in Table 4. In Fig. 1 the Δh_v function is plotted *versus* \bar{n} .

It is possible to get the total reaction heat of the fourth complex by titrations of cadmium(II) into an excess of cyanide. The compositions of the solutions S and T for these measurements were:



The dilution heats of the ligand were determined by titrations of 3 M NaClO_4 into S_2 , and the dilution heats of the central ion could be neglected as before. For the data see Table 2, where corresponding values of v , amount of Cd^{2+} ,

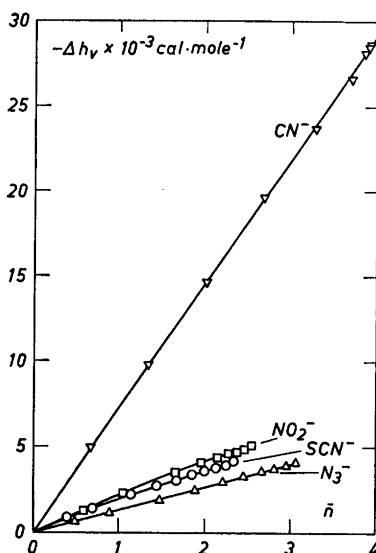


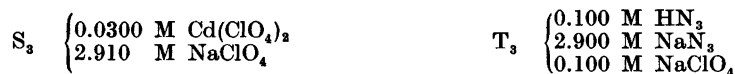
Fig. 1. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the cadmium cyanide, azide, thiocyanate, and nitrite systems.

Table 4. The reaction heats, corrected for dilution, obtained at the titrations of the CN^- , N_3^- , SCN^- , and NO_2^- systems. For each system two series are performed. C_{Cd} is the initial cadmium ion concn. in the S solutions.

Ligand	$\sum Q_{\text{corr.}} \text{ (cal)}$							
	CN^-		N_3^-		SCN^-		NO_2^-	
$C_{\text{Cd}}(\text{M})$	0.006		0.030		0.030		0.030	
$v \text{ (ml)}$								
1.005			1.75	1.73	2.24	2.24	3.69	3.72
2.009	2.95	2.95	3.24	3.23	3.96	3.94	6.63	6.65
4.018	5.86	5.82	5.61	5.57	6.34	6.34	10.19	10.19
6.027	8.80	8.73	7.43	7.39	7.94	7.97	12.01	12.03
8.036	11.76	11.70	8.81	8.76	9.10	9.16	13.09	13.13
10.045	14.24	14.12	9.78	9.73	10.00	10.05	13.77	13.78
12.054	16.03	15.81	10.62	10.58	10.72	10.76	14.28	14.28
14.063	16.89	16.78	11.32	11.28	11.29	11.35	14.70	14.72
16.072	17.17	16.98	11.93	11.91		11.86	15.02	15.02
18.081	17.25	17.06	12.45	12.43		12.32	15.29	15.30

Q_x , $Q_{\text{dil.}}$, $Q_{\text{corr.}}$, $\sum Q_{\text{corr.}}$, and Δh_v are given. From these measurements the $\sum_{k=1}^4 \Delta H_k$ was found to be $29.4 \text{ kcal.mole}^{-1}$, a value in good agreement with that of the other titrations (see Table 5). The calculations using the stability constants of Leden¹⁰ and of Flengas¹⁶ gave very similar enthalpy values. To obtain a still better accordance with the calorimetric data, a corrected set of complex constants has also been tried. For the results see Table 5.

The cadmium(II) azide system. In the literature there are reported both four¹⁰ and five¹⁷ mononuclear complexes between the cadmium and the azide ion. The stability constants reported by Leden¹⁰ are more closely in agreement with the calorimetric measurements and have been used here with a slight correction (see Table 5). To avoid hydrolysis during the titrations, the ligand solution was a buffer and the compositions of S and T were:



The dilution heats of the ligand were determined by titrations of T_3 into 3.000 M NaClO_4 . Corresponding values of v and $Q_{\text{dil.}}$ have been collected in Table 3 and of v and $\sum Q_{\text{corr.}}$ in Table 4. In Fig. 1 the Δh_v function is plotted *versus* \bar{n} . When the correction:

$$Q_x - Q_{\text{dil.}} = Q_{\text{corr.}} \quad (4)$$

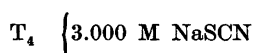
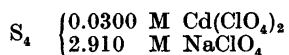
is made, allowance must be taken for the complex formation, and $Q_{\text{dil.}}$ is thus calculated for the dilution of the ligand to the actual concentration of the free ligand remaining in the equilibrated solution.

The cadmium(II) thiocyanate system. The results given in the literature⁹ for the stability constants of this system vary, why a potentiometric determina-

Table 5. Enthalpy values for the four studied systems using different sets of β_j values. A: $-\left(\sum_{k=1}^j \Delta H_k^\circ \pm \sigma \sum_{k=1}^j \Delta H_k^\circ\right) \times 10^{-3}$ cal.mole $^{-1}$.

Ref.	The CN $^-$ system			Ref.	The N $_3^-$ system		
	β_j (M $^{-j}$)	A	σ Q $_{\text{corr.}}$ (cal)		β_j (M $^{-j}$)	A	σ Q $_{\text{corr.}}$ (cal)
10	3×10^5	7.12 ± 0.44	0.1700	10	41	1.09 ± 0.05	0.0592
	4×10^{10}	15.02 ± 0.48			600	2.65 ± 0.11	
	1.7×10^{15}	21.85 ± 0.36			1700	3.93 ± 0.36	
	6×10^{18}	28.04 ± 0.31			8000	5.44 ± 0.19	
16	1.5×10^5	7.35 ± 0.24	0.1102	17	25	1.42 ± 0.05	0.0509
	4.0×10^9	15.13 ± 0.48			400	2.47 ± 0.10	
	8.5×10^{13}	22.15 ± 0.27			800	5.56 ± 0.41	
	1.3×10^{17}	29.07 ± 0.27			3000	5.24 ± 0.24	
	3×10^5	7.39 ± 0.25	0.1083		42	1.15 ± 0.04	0.0587
	4×10^{10}	15.12 ± 0.27			560	2.56 ± 0.09	
	1.4×10^{15}	22.24 ± 0.21			1900	4.22 ± 0.26	
	2×10^{18}	29.27 ± 0.23			7000	5.49 ± 0.18	
Ref.	The SCN $^-$ system			Ref.	The NO $_2^-$ system		
	β_j (M $^{-j}$)	A	σ Q $_{\text{corr.}}$ (cal)		β_j (M $^{-j}$)	A	σ Q $_{\text{corr.}}$ (cal)
10	24.5	2.12 ± 0.04	0.0511	10	63	2.10 ± 0.05	0.0866
	96	3.95 ± 0.13			1020	4.25 ± 0.10	
	380	5.11 ± 0.11			6500	5.46 ± 0.10	
11	26	2.03 ± 0.03	0.0424		58	2.09 ± 0.03	0.0482
	150	3.35 ± 0.05			1200	4.25 ± 0.04	
	500	5.43 ± 0.13			5000	5.78 ± 0.06	
11	26	1.94 ± 0.01	0.0175				
	175	3.67 ± 0.05					
	300	5.24 ± 0.19					
	300	6.28 ± 0.17					

tion of the system was made.¹¹ In the calculations of the enthalpy values different sets of constants were used to see whether a postulated maximum of 3 or 4 ligands per central metal ion gave the more reasonable fit to the experimental data. The results are given in Table 5. The compositions of the solutions S and T were:



The dilution heats were determined as before, and the complex formation was accounted for. For the experimental data see Tables 3 and 4. In Fig. 1 the Δh_v function is plotted *versus* \bar{n} .

Table 6. The differences ($Q_{\text{corr.}} - Q_{\text{corr., calc.}}$) for the CN^- , N_3^- , SCN^- , and NO_2^- systems. For each system two series are tabulated, and the β_j values used at the calculations are those finally chosen.

Ligand	$(Q_{\text{corr.}} - Q_{\text{corr., calc.}})$ (cal)							
	CN^-		N_3^-		SCN^-		NO_2^-	
c_{Cd} (M)	0.006		0.030		0.030		0.030	
v (ml)								
1.005			0.003	-0.017	0.011	0.011	0.016	-0.054
2.009	-0.044	-0.044	-0.006	0.014	-0.001	-0.021	0.072	0.052
4.018	-0.103	-0.143	0.023	-0.007	-0.018	-0.008	-0.025	-0.045
6.027	-0.042	-0.082	0.053	0.053	-0.022	0.028	-0.031	-0.011
8.036	0.056	0.075	-0.007	-0.017	-0.013	0.007	-0.009	0.021
10.045	-0.149	-0.198	-0.133	-0.133	-0.008	-0.016	-0.017	-0.047
12.054	0.025	-0.085	-0.040	-0.020	-0.008	-0.020	0.034	0.014
14.063	0.186	0.286	-0.006	-0.006	-0.034	-0.014	0.062	0.082
16.072	0.053	-0.017	0.040	0.060		-0.000	0.046	0.026
18.081	-0.022	-0.022	0.056	0.056		0.022	0.043	0.063

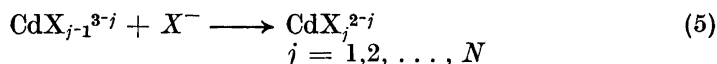
The cadmium(II) nitrite system. Even for this system, different stability constants are published,⁹ but the best agreement was found using those reported by Leden,¹⁰ adjusted to give the best fit to the calorimetric data. The compositions of the solutions S and T were:



The dilution heats were determined as before and the complex formation was accounted for. For the data see Tables 3 and 4. In Fig. 1 the Δh_v function is plotted *versus* \bar{n} . The influence of the stability constants on the enthalpy changes has been examined by using different sets of constants (see Table 5). The results from the calculations suggest four complexes in accordance with the three other systems (see Table 6), although it is difficult to estimate the strength of the fourth complex from the measurements.

With the exception of the cyanide system, these systems are rather weak and so the accuracy for the higher complexes is lower. To obtain the best possible results, different sets of stability constants were used during the calculations to minimize the error square sum. In one case, the thiocyanate system, the constants have been measured by a potentiometric method,¹¹ and the new values verified those indicated by the calorimetric data (see Table 5). Thus it is possible to check the stability constants by calorimetric measurements.

The enthalpy changes for the stepwise reactions:



may be calculated from the experimental values collected in Tables 2–4, using the methods just mentioned. These values, together with corresponding

Table 7. The stability constants used and the computed values of free energy, enthalpy, and entropy changes for the stepwise reactions of the four cadmium pseudo halide systems are tabulated. The ΔH_j° values with their computed standard deviations. The β_j , ΔG_j° , and ΔS_j° values with their estimated errors.

Ligand		CN ⁻	N ₃ ⁻	SCN ⁻	NO ₂ ⁻
β_j (M ^{-j})	$j = 1$	$(3 \pm 1) \times 10^5$	42 ± 2	26 ± 1	58 ± 3
	2	$(4 \pm 1) \times 10^{10}$	560 ± 60	175 ± 15	1200 ± 200
	3	$(14 \pm 4) \times 10^{14}$	1900 ± 400	300 ± 50	2000 ± 1000
	4	$(2 \pm 1) \times 10^{18}$	7000 ± 2000	300 ± 100	
$-\Delta G_j^\circ \times 10^{-3}$ (cal.mole ⁻¹)	1	7.47 ± 0.24	2.21 ± 0.03	1.93 ± 0.02	2.41 ± 0.03
	2	6.99 ± 0.29	1.54 ± 0.08	1.13 ± 0.07	1.80 ± 0.12
	3	6.20 ± 0.26	0.72 ± 0.16	0.32 ± 0.12	0.85 ± 0.17
	4	4.31 ± 0.45	0.77 ± 0.25	0.00 ± 0.26	
$-\Delta H_j^\circ \times 10^{-3}$ (cal.mole ⁻¹)	1	7.39 ± 0.25	1.15 ± 0.04	1.94 ± 0.01	2.09 ± 0.03
	2	7.73 ± 0.35	1.41 ± 0.10	1.73 ± 0.06	2.11 ± 0.07
	3	7.12 ± 0.34	1.66 ± 0.27	1.57 ± 0.20	1.58 ± 0.10
	4	7.03 ± 0.31	1.27 ± 0.32	1.04 ± 0.41	
ΔS_j° (cal.mole ⁻¹ degree ⁻¹)	1	0.3 ± 1.3	3.5 ± 0.2	0.0 ± 0.1	1.1 ± 0.2
	2	-2.5 ± 1.6	0.2 ± 0.4	-2.0 ± 0.4	-1.0 ± 0.5
	3	-3.1 ± 1.4	-3.1 ± 1.1	-4.2 ± 0.8	-2.4 ± 0.6
	4	-9.1 ± 1.8	-1.7 ± 1.3	-3.5 ± 1.6	

values of free energy and entropy changes, have been collected in Table 7, and can be compared with those in Table 1.

Accuracy of the results. The error in $Q_{\text{corr.}}$ depends upon the two measured values of Q_x and $Q_{\text{dil.}}$, which are reproduced to better than ± 0.02 cal, with the exception of the cyanide system, for which the random errors are greater. In Table 6 are given the values of the difference ($Q_{\text{corr.}} - Q_{\text{corr., calc.}}$) for the four systems. Only small systematic errors are found, possibly depending upon an incorrectly made correction for the dilution heats, or on deviations in the complex constants. Usually, the magnitude of the differences is that expected from the accuracy of the calorimeter. The error in the enthalpy changes, however, also depends upon the accuracy of the stability constants, but calculations using different sets of constants give relatively small variations in the ΔH_j° values (see Table 5). From the errors in the free energy change given in the literature and the standard deviation in the enthalpy term, the uncertainty in the corresponding entropy term has been estimated.

DISCUSSION

The complex systems investigated here have not previously been studied systematically by calorimetric methods. The enthalpy values, however, of the thiocyanate systems given by Golub *et al.*^{3,4} and of the cyanide systems re-

ported by Christensen *et al.*⁶⁻⁸ all have the same trends as those found in this work (see Tables 1 and 7).

The four systems studied may be divided into two groups: one consisting of the strong cadmium cyanide system, the other of the weak cadmium azide, thiocyanate, and nitrite systems. In eqn. (2) the free energy change, a function of the stability constant for the complex reaction, is split up into one enthalpy and one entropy term. The difference in stability between the two groups is caused by the enthalpy term, since the entropy term is of the same order for all four systems. In no instance the entropy term is of great importance for the complex formation, although the small differences in stability within the weak group can be partially related to this term.

For each of the pseudo halide systems, the $-\Delta G_j^\circ$ and ΔS_j° values decrease progressively as j increases, whilst the $-\Delta H_j^\circ$ values are surprisingly constant. The patterns of the cadmium halide systems are quite different, having irregular enthalpy and entropy values which influence the stability of these systems and cause the particularly weak second step.²

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