# Thermochemical Studies on Metal Complexes

VII. Free Energy, Enthalpy, and Entropy Changes for Stepwise Formation of Cadmium(II) Chloride and Iodide Complexes at Different Ionic Strengths

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The enthalpy changes for the stepwise reactions:

$$CdA_{j-1}^{3-j} + A^- \longrightarrow CdA_j^{2-j}$$
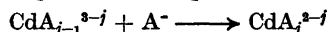
where A^- is the chloride or iodide ion, have been determined at different ionic strengths by a calorimetric titration procedure. From these enthalpy changes and the changes of free energy, computed from the stability constants, the entropy changes have been calculated from the relation:

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

The measurements were performed in aqueous sodium perchlorate media, the total equivalent concentration of all ions being constant, $I' = 0.25, 0.50, 1.00,$ and 2.00 (M), and at $25.00°C$. No general systematic trend was found for the enthalpy and entropy terms of the investigated systems when the ionic strength was varied.

In several investigations ionic strength has been found to influence the complex formation of a number of systems in the same way.[1-5] This means that the changes in activity coefficients are similar for the different systems and may also indicate a similar structure of the species involved. A better physical interpretation may be obtained by splitting up the free energy change into one enthalpy and one entropy term according to the relation:

$$\Delta G_j^\circ = \Delta H_j^\circ - T \Delta S_j^\circ \tag{1}$$

and determining these two terms at some different ionic strengths. Earlier, the protonation of the acetate ion has been studied at different ionic strengths by Eva Hansson [6,7] using a calorimetric method and the enthalpy change, $-\Delta H_{11}^\circ$, was found to increase with increasing ionic strength. Vanderzee and Dawson [1] obtained the same result for the formation of the cadmium(II) chloride complex species from potentiometric measurements of the stability constants at different temperatures.

In a previous potentiometric investigation some cadmium(II) complex systems [5] have been studied and the stability constants determined. In this paper the calorimetric determination of the enthalpy changes of the formation of cadmium(II) chloride and iodide complex species is reported. The stability constants used in the present work have been taken from the literature (the cadmium(II) chloride system investigated by Vanderzee and Dawson [1]) or were those determined earlier at this laboratory (the cadmium(II) iodide system [5]). From these constants, the concentrations of the various complex species in the solutions studied and the changes in free energy have been computed. The calorimetric determinations of the reaction heats were made using a reaction calorimeter and a titration procedure described earlier.[8] The measurements were carried out at 25.00°C, and in aqueous sodium perchlorate media, the total equivalent concentration of all ions being constant (see Ref. 5), $I'=0.25$, 0.50, 1.00, and 2.00 (M). The values obtained were combined with the results at $I=3.00$ (M) from previous measurements.[9]

The calculations of the enthalpy values from the titration data and a list of most of the symbols and equations used were described in a previous paper.[9] A least squares program developed by Sillén et al.[10,11] and the high speed computer IBM 7090 at NEUCC in Copenhagen were used. The results obtained in this way were checked with special experiments at high ligand concentrations, which gave better enthalpy values for the third and fourth steps,[5] using the equation:

$$\Delta h_v = \sum_{j=1}^{N} \sum_{k=1}^{j} \alpha_j \times \Delta H_k^\circ \tag{2}$$

α_j was determined from the equilibrium constants and ΔH_1° and ΔH_2° taken from the values calculated by the high speed computer.

EXPERIMENTAL

Chemicals. Cadmium(II) perchlorate, sodium perchlorate, and *ligand solutions* were prepared and analysed as previously.[5,9] To suppress hydrolysis the pH of the cadmium solutions was maintained at 4−5. All chemicals were of analytical grade and for the preparations of solutions and the performance of titrations only calibrated volumetric flasks, burettes, and pipettes were used.

Procedure. The calorimeter and the titration procedure used were the same as described in a previous paper.[8] This calorimeter was equipped with a device for the successive addition of known amounts of 2 or 5 ml portions up to a total of 25 ml of a titrant, T, into a calorimeter solution, S, initial volume 100.0 ml. The compositions of the solutions S and T were:

$$S\begin{cases} C_{Cd} & M\ Cd(ClO_4)_2 \\ (I'-2\ C_{Cd}) & M\ NaClO_4 \end{cases} \qquad T\begin{cases} C_A & M\ NaA \\ (I'-C_A) & M\ NaClO_4 \end{cases}$$

$$A^- = Cl^-\ or\ I^-$$

or, for the measurements at high ligand concentrations:

$$S\begin{cases} C_A & M\ NaA \\ (I'-C_A) & M\ NaClO_4 \end{cases} \qquad T\begin{cases} C_{Cd} & M\ Cd(ClO_4)_2 \\ (I'-2\ C_{Cd}) & M\ NaClO_4 \end{cases}$$

Each titration series was repeated at least once.

The dilution heats of the ligands were determined by similar titration series without cadmium perchlorate in the solutions. For the central ion no effect was found upon diluting from $C_{Cd} = 0.050$ (M) to $C_{Cd} = 0.001$ (M) and it was assumed that the dilution heats of the central ion and of the various complexes could be neglected at all ionic strengths.

The thermodynamic standard state for the solute species M, A, and MA_j, where M is the central ion and A the ligand, is in this study a temperature of 25.00°C and a hypothetically ideal one molar solution with neutral salt such that the total equivalent concentration of all ions is constant and equal to I'.[5] 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 [8] gave a linear dependence of the heat equivalent of the calorimetric system upon the total amount of titrant added. By use of a least squares method, the results were described by the relation:

$$-\varepsilon_v = l + kv \tag{3}$$

where the constants l and k are given in Table 1. l depends on the ionic strength and the pipette used while k is constant within the accuracy of the measurements. The accuracy of the ε_v-function is better than $\pm 5 \times 10^{-3}$ cal·ohm^{-1} in the range $0 < v < 30$ (ml).

The cadmium(II) chloride system. From a potentiometric investigation by Vanderzee and Dawson [1] two or three mononuclear complex species were found to be formed at the ionic strengths and concentration ranges used. The stabilities of the complex species are so low that the ligand concentration range must be extended as high as possible. For that reason the titration series were performed in two ways. In titrations of type I the central ion was supplied by solution S and the ligand by solution T. The concentrations were at $I' = 0.25$ (M); $C_{Cd} = 0.0250$ (M) and $C_{Cl} = 0.250$ (M); at $I' = 0.50$ (M): $C_{Cd} = 0.0250$ (M), $C_{Cl} = 0.500$ (M); at $I' = 1.00$ and 2.00 (M): $C_{Cd} = 0.0500$ (M), $C_{Cl} = 1.000$ (M). The dilution heats of the ligand were determined as described above and corresponding values of v and Q_{dil} are collected in Table 2. The

Table 1. The different values of the constants l and k in the relation $-\varepsilon_v = l + kv$.

I' (M)	Pipette volume (ml)	Cl$^-$		I$^-$	
		k	l	k	l
0.25	2	—	—	0.0197	2.180
	5	—	—	0.0197	2.212
0.5	2	—	—	0.0197	2 161
	5	0.0196	2.184	0.0197	2.192
1	2	—	—	0.0197	2.130
	5	0.0196	2.170	0.0197	2.162
2	2	—	—	0.0197	2.102
	5	0.0196	2.159	0.0197	2.133

Table 2. The dilution heats, $Q_{dil.}$, for portions of 5.02 ml of the different chloride solutions, T, added to 100.0 ml I' M $NaClO_4$ solutions.

v (ml)	$Q_{dil.}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
5.02	0.016	−0.007	−0.057	−0.048	−0.175	−0.175	0.000	−0.014
10.05	0.030	0.034	−0.052	−0.079	−0.170	−0.137	0.000	−0.005
15.07			−0.072	−0.069	−0.143	−0.141	−0.010	−0.015
20.09			−0.070	−0.044	−0.159	−0.154	−0.026	0.005
25.11			−0.037	−0.062	−0.107	−0.109	0.011	0.011

measured values Q_X are corrected for the dilution heats according to the equation:

$$Q_X - Q_{dil.} = Q_{corr.} \qquad (4)$$

where $Q_{dil.}$ is taken from the corresponding addition in the dilution series. The effect of complex formation on the dilution heat in measurements of Q_X could be neglected. The corresponding values of v and $Q_{corr.}$ are given in Table 3.

In titrations of type II the ligand was supplied by solution S and the central ion by solution T, which gave a much higher final concentration of the ligand. The concentrations were at $I'=0.50$ (M): $C_{Cd}=0.0250$ (M) and $C_{Cl}=0.125$ and 0.250 (M); at $I'=1.00$ and 2.00 (M): $C_{Cd}=0.0500$ (M), $C_{Cl}=0.250$ and 0.500 (M). The dilution heats were determined and the corrections performed as above. The corresponding values of v, $Q_{dil.}$, and $Q_{corr.}$ are tabulated in Table 4. The values of β_j used and $-\Delta G_j^\circ$, $-\Delta H_j^\circ$, and ΔS_j° for the different ionic strengths are collected in Table 8.

The cadmium(II) iodide system. In a previous paper [5] the results from a potentiometric investigation were reported. The second species was found to be comparatively unstable at all the ionic strengths used, for which reason the stepwise enthalpy changes for the second and third reactions must be uncertain. At all ionic strengths four complex species could describe the

Table 3. The total reaction heats corrected for dilution, $\sum Q_{corr.}$, obtained in the titrations of the chloride system at different ionic strengths.

v (ml)	$\sum Q_{corr.}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
5.02	−0.087	−0.100	−0.209	−0.190	−0.351	−0.331	−0.030	−0.025
10.05	−0.184	−0.209	−0.364	−0.341	−0.668	−0.631	−0.127	−0.119
15.07			−0.466	−0.465	−0.937	−0.905	−0.337	−0.329
20.09			−0.567	−0.556	−1.135	−1.113	−0.573	−0.598
25.11			−0.659	−0.634	−1.367	−1.337	−0.840	−0.851

Table 4. The heats of dilution, $Q_{\text{dil.}}$, and reaction corrected for dilution, $Q_{\text{corr.}}$, obtained in the titrations of chloride solutions, S, by I' M $NaClO_4$ solutions and central ion solutions, T, respectively. At $I'=0.5$ (M) $a=0.125$ (M) and at $I'=1$ and 2 (M) $a=0.250$ (M).

I' (M)	v (ml)	$C_{\text{NaCl}}=a$ (M)		$C_{\text{NaCl}}=2a$ (M)	
		$Q_{\text{dil.}}$ (cal)	$Q_{\text{corr.}}$ (cal)	$Q_{\text{dil.}}$ (cal)	$Q_{\text{corr.}}$ (cal)
0.5	5.02	-0.039	-0.048	-0.023	-0.048
	10.05	-0.021	-0.029	-0.031	-0.065
	15.07	-0.010	-0.034	-0.022	-0.054
1	5.02	-0.027	-0.077	-0.052	-0.111
	10.05	-0.031	-0.072	-0.061	-0.104
	15.07	-0.002	-0.034	-0.054	-0.098
2	5.02	0.005	-0.070	0.002	-0.134
	10.05	0.005	-0.063	0.002	-0.119
	15.07	-0.005	-0.041	-0.015	-0.114

potentiometric data [5] and on the basis of these and the earlier measurements at $I=3.00$ (M) [9] only mononuclear species are assumed. To obtain as large a ligand concentration range as possible the titration series for this system also were performed in two ways. The concentrations of the central ion and ligand in the titrations of type I were at $I'=0.25$ (M): $C_{\text{Cd}}=0.0250$ (M), $C_{\text{I}}=0.250$ (M); $I'=0.50$ (M): $C_{\text{Cd}}=0.0250$ (M), $C_{\text{I}}=0.500$ (M); $I'=1.00$ and 2.00 (M): $C_{\text{Cd}}=0.0500$ (M), $C_{\text{I}}=1.000$ (M). The corresponding values of v and $Q_{\text{dil.}}$ are collected in Table 5 and of v and $Q_{\text{corr.}}$ in Table 6.

In titrations of type II the concentrations were at $I'=0.25$ (M): $C_{\text{Cd}}=0.0250$ (M), $C_{\text{I}}=0.125$ (M); $I'=0.50$ (M): $C_{\text{Cd}}=0.0250$ (M), $C_{\text{I}}=0.250$ (M); $I'=1.00$ and 2.00 (M): $C_{\text{Cd}}=0.0500$ (M), $C_{\text{I}}=0.500$ (M). The dilution heats were deter-

Table 5. The dilution heats, $Q_{\text{dil.}}$, for portions of 2.009 ml of the different iodide solutions, T, added to 100.0 ml I' M $NaClO_4$ solutions.

v (ml)	$Q_{\text{dil.}}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
2.01	0.033	0.024	0.008	0.002	-0.024	-0.020	0.000	0.006
4.02	0.023	0.016	0.016	0.011	-0.035	-0.002	0.009	0.002
6.03	0.032	0.009	0.023	-0.002	-0.025	-0.016	0.009	0.004
8.04	0.014	0.014	0.046	0.046	-0.014	-0.007	0.014	0.016
10.05	0.040	0.031	-0.024	0.005	-0.009	-0.012	0.007	0.009
12.05	0.041	0.017	0.012	0.007	-0.019	-0.002	0.007	-0.002
14.06	0.025	0.022	0.007	0.027	-0.010	0.000	0.012	0.012
16.07	0.027	0.037	0.007	0.017	-0.005	0.000	0.007	0.010
18.08	0.035	0.023	0.005	0.008	-0.005	-0.010	0.017	0.005
20.09	0.026	0.018	0.003	0.015	-0.013	-0.005	-0.002	0.005

Table 6. The total reaction heats, corrected for dilution, $\sum Q_{corr.}$, obtained in the titrations of the iodide system at different ionic strengths.

v (ml)	$\sum Q_{corr.}$ (cal)							
	$I'=0.25$ (M)		$I'=0.5$ (M)		$I'=1$ (M)		$I'=2$ (M)	
2.009	0.774	0.759	1.427	1.445	3.528	3.515	3.500	3 506
4 018	1.456	1.441	2.578	2.591	6.349	6.305	6.245	6.269
6.027	2.041	2.037	3.407	3.520	8.711	8.665	8.541	8.590
8.036	2.568	2.553	4.230	4.347	10.91	10.88	10.68	10.77
10.045	3.032	3.000	5.015	5.125	13.12	13.05	12.81	12.92
12.054	3.461	3.423	5.775	5.897	15.31	15.25	14.95	15.07
14.063	3.867	3.826	6.523	6.640	17.48	17.40	17.06	17.21
16.072	4.210	4.179	7.276	7.296	19.60	19.54	19.15	19.31
18.081	4.544	4.518	8.019	8.136	21.68	21.60	21.18	21.35
20.09	4.878	4.852	8.738	8.868	23.65	23.57	23.11	23.27

mined and the corrections performed as above. The corresponding values of v, $Q_{dil.}$, and $Q_{corr.}$ are tabulated in Table 7. The values of β_j used and $-\Delta G_j^\circ$, $-\Delta H_j^\circ$, and ΔS_j° for the different ionic strengths are collected in Table 8.

DISCUSSION

For the chloride system the values of the enthalpy changes at different ionic strengths obtained in this work are in fair agreement with those determined by Vanderzee and Dawson,[1] specially in view of the method used in

Table 7. The heats of dilution, $Q_{dil.}$, and reaction corrected for dilution, $Q_{corr.}$, obtained in the titrations of iodide solutions, S, by I' M $NaClO_4$ solutions and central ion solutions, T, respectively.

I' (M)	v (ml)	$Q_{dil.}$ (cal)	$Q_{corr.}$ (cal)
0.25	5.02	−0.005	0.820
	10.05	0.012	0.736
	15.07	−0.005	0.708
0.5	5.02	−0.009	0.901
	10.05	0.005	0.917
	15.07	0.022	0.872
1	5.02	−0.005	1.964
	10.05	−0.012	1.936
	15.07	0.007	1.933
2	5.02	−0.007	1.820
	10.05	−0.014	1.803
	15.07	0.000	1.782

Table 8. The stability constants used and the computed values of free energy, enthalpy, and entropy changes for the stepwise reactions of the cadmium chloride and iodide complex systems at different ionic strengths. The $\Delta H_j°$-values with their computed standard deviations, the β_j, $\Delta G_j°$, and $\Delta S_j°$-values with their estimated errors. The values at ionic strength 3 M are taken from Ref. 9. ᵃValues extrapolated by the method of Vanderzee and Dawson.[1]

Ligand	Γ (M)	j	0.25	0.5	1	2	$I=3$
Cl⁻	β_j (M⁻ʲ)	1	28 ±3ᵃ	23.5± 0.2	22.3 ± 0.2	26.5 ± 0.3	38.5 ±1
		2	80 ±10ᵃ	63	60 ± 2	89 ± 3	170 ±10
		3		—	26 ± 2	61 ± 5	260 ±10
	$-\Delta G_j° \times 10^{-3}$ (cal mole⁻¹)	1	1.97± 0.06	1.87± 0.01	1.84± 0.01	1.94± 0.01	2.16± 0.02
		2	0.62± 0.08	0.58± 0.02	0.59± 0.02	0.72± 0.02	0.88± 0.05
		3			−0.50± 0.05	−0.22± 0.05	0.25± 0.06
	$-\Delta H_j° \times 10^{-3}$ (cal mole⁻¹)	1	−0.21± 0.02	−0.25± 0.01	−0.13± 0.01	0.00± 0.01	0.10± 0.01
		2		−0.67± 0.12	−0.49± 0.04	−0.34± 0.03	−0.02± 0.02
		3			−1.8 ± 0.5	−1.93± 0.17	−1.85± 0.05
	$\Delta S_j°$ (cal mole⁻¹ degree⁻¹)	1	7.3 ± 0.2	7.1 ± 0.1	6.6 ± 0.1	6.5 ± 0.1	6.9 ± 0.1
		2		4.2 ± 0.4	3.6 ± 0.2	3.6 ± 0.1	3.0 ± 0.2
		3		—	4.3 ± 1.7	5.7 ± 0.6	7.0 ± 0.3
I⁻	β_j (M⁻ʲ)	1	88 ± 1	77 ± 1	75 ± 1	94 ± 1	121 ± 2
		2	440 ± 100	430 ± 100	450 ± 100	400 ± 200	600 ± 200
		3	$(2.1 ± 0.2) \times 10^4$	$(1.9 ± 0.1) \times 10^4$	$(2.2 ± 0.2) \times 10^4$	$(5.1 ± 0.3) \times 10^4$	$(8.2 ± 0.5) \times 10^4$
		4	$(3.2 ± 0.3) \times 10^5$	$(3.1 ± 0.2) \times 10^5$	$(4.2 ± 0.2) \times 10^5$	$(11 ± 1) \times 10^5$	$(33 ± 2) \times 10^5$
	$-\Delta G_j° \times 10^{-3}$ (cal mole⁻¹)	1	2.65± 0.01	2.57± 0.01	2.56± 0.01	2.69± 0.01	2.84± 0.01
		2	0.95± 0.15	1.02± 0.16	1.06± 0.15	0.86± 0.41	0.95± 0.24
		3	2.29± 0.16	2.24± 0.16	2.30± 0.16	2.87± 0.41	2.91± 0.25
		4	1.61± 0.08	1.65± 0.05	1.75± 0.07	1.82± 0.07	2.19± 0.06
	$-\Delta H_j° \times 10^{-3}$ (cal mole⁻¹)	1	2.32± 0.02	2.43± 0.02	2.45± 0.01	2.32± 0.01	2.26± 0.01
		2	1.7 ± 0.6	0.93± 0.36	0.48± 0.24	0.29± 0.31	0.20± 0.12
		3	—	0.75± 0.49	1.38± 0.27	1.21± 0.34	0.73± 0.14
		4	—	4.23± 0.42	3.98± 0.16	3.80± 0.15	3.81± 0.03
	$\Delta S_j°$ (cal mole⁻¹ degree⁻¹)	1	1.1 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	1.2 ± 0.1	1.9 ± 0.1
		2	−2.5 ±2	0.3 ± 1.1	1.9 ± 0.9	1.9 ± 1.7	2.5 ± 0.9
		3	—	5.0 ± 1.7	3.1 ± 1.0	5.6 ± 1.8	7.3 ± 1.0
		4	—	−8.7 ± 1.4	−7.5 ± 0.6	−6.6 ± 0.6	−5.4 ± 0.2

that work, *viz.* potentiometric measurements of the stability constants at different temperatures. For the iodide system no systematic investigation of the enthalpy changes at different ionic strengths has been found in the literature.*

Contrary to the free enery change, which varies in the same way with the ionic strength for both systems studied here, there is no uniformity of the enthalpy and entropy changes. For the chloride system $-\Delta H_1^\circ$ and $-\Delta H_2^\circ$ increase with increasing ionic strength, while ΔS_1° goes through a minimum and ΔS_2° decreases. For the iodide system $-\Delta H_1^\circ$ and $-(\Delta H_2^\circ + \Delta H_3^\circ)$ go through a maximum and $-\Delta H_4^\circ$ decreases with increasing ionic strength. ΔS_1° goes through a minimum and $(\Delta S_2^\circ + \Delta S_3^\circ)$ and ΔS_4° increase (see Table 8). However, the variations are such that no physical explanations can be made at this stage.

A calorimetric investigation of the cadmium(II) thiocyanate and acetate complex systems at different ionic strengths is also performed and the results from these measurements will be presented in a subsequent paper.

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* After this investigation was finished we were kindly informed by Professor Vanderzee about unpublished values of the enthalpy changes of the cadmium(II) iodide system obtained at different ionic strengths by Vanderzee and Myers[12] through potentiometric measurements of the stability constants at different temperatures. The values obtained were:

I' (M)	0.2	0.5	1.0	2.0	3.0
$-\Delta H_1 \times 10^{-3}$ (cal mole^{-1})	2.52	2.17	2.30	2.30	2.00
$-\Delta H_2 \times 10^{-3}$ (cal mole^{-1})	0.97	1.44	0.40	0.00	0.20
$-\Delta H_3 \times 10^{-3}$ (cal mole^{-1})	0.23	−0.64	0.30	0.20	0.50
$-\Delta H_4 \times 10^{-3}$ (cal mole^{-1})	4.29	5.38	4.60	4.50	3.60

The agreement between the values obtained by the calorimetric method reported here and those determined by Vanderzee and Myers is surprisingly good (see Table 8).