

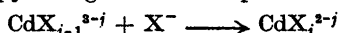
Thermochemical Studies on Metal Complexes

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

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The enthalpy changes for the stepwise reactions:



where X^- is fluoride, chloride, bromide, or iodide ion, have been determined by means of a specially developed calorimetric titration procedure.¹

From these enthalpy changes and the changes in free energy, computed from known stability constants, the entropy changes can be calculated from the relation:

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

All data, except for some of the fluoride measurements, refer to an aqueous sodium perchlorate medium of ionic strength 3.00 M and a temperature of 25.00°C.

In the four systems the variation with j of the free energy, enthalpy, and entropy changes is similar. The increasing stability from fluoride to iodide has been found to depend on the variation of the enthalpy term. The entropy term, however, is of great importance for the formation of some of the complex species.

The complex formation of the four cadmium(II) halide systems in aqueous solution is well known from many measurements of the stability constants.² Since the cadmium ion is a class (b)³ or "soft" acceptor⁴ the stability of its halide complexes increases from fluoride to iodide, which depends on a rising degree covalent bond. The changes in free energy are related to the stability constants by the eqn.:

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

and are then found to vary in the same way as the stability constants.

The stabilities of complexes are governed not only by the enthalpy change, but often to a great extent by entropy factors.^{5,6} Thus, in recent years, the

Table 1. Comparison of reported values of thermodynamic properties of the cadmium halide systems. The values of the overall standard changes are given. Method to determine the enthalpy change: var. = from equilibrium measurements at different temperatures; dil. = from calorimetric dilution measurements of salt solutions; cal. = from calorimetric measurements with direct titrations. (Ref. 11 reports 6 complex steps for the cadmium-iodide system).

Ligand	Cl ⁻				Br ⁻			I ⁻			
	7	8	9	10	9	10	10	10	11	12	13
Ref.											
Method	var.	var.	var.	dil.	var.	dil.	dil.	dil.	var.	cal.	cal.
Ionic strength	3	3	4.5	0	4.5	0	0	0	3	—	2
$-\sum_{k=1}^j \Delta G_k^\circ \times 10^{-3}$ (cal.mole ⁻¹)	1	2.10	1.80	2.67	2.30	2.93	3.34	2.20	2.88		
	2	3.0	3.03	—	3.30	—	—	3.51	3.70		
	3	3.3	3.12	—	4.40	—	—	6.12	6.37		
	4	—	—	2.53	—	5.10	—	7.34	8.4	6.91	
$-\sum_{k=1}^j \Delta H_k^\circ \times 10^{-3}$ (cal.mole ⁻¹)	1	-0.6	0.05	-0.98	-2.30	0.32	2.05	10.4	2.32		
	2	1.1	-0.65	—	2.00	—	—	11.5	-1.13		
	3	-4.7	-2.84	-2.90	0.00	—	—	13.0	6.52		
	4	—	—	0	—	2.60	—	17.0	10.8	7.95	
$\sum_{k=1}^j \Delta S_k^\circ$ (cal.mole ⁻¹ , degree ⁻¹)	1	8.5	6.9	12.2	15.4	8.8	4.3	-27.3	1.88		
	2	6.4	12.2	—	4.3	—	—	-26.7	16.20		
	3	26.5	20.1	18.4	14.7	—	—	-23.0	-0.50		
	4	—	—	26.1	—	25.8	—	-32.0	-3.49		

importance of breaking up the change in free energy into one enthalpy and one entropy term according to the eqn.:

$$\Delta G_i^\circ = \Delta H_i^\circ - T\Delta S_i^\circ \quad (2)$$

has grown more and more evident.

So far very few investigations of the enthalpy changes of these systems have been published.⁷⁻¹³ A summary of these results is collected in Table 1, which gives corresponding values of free energy, enthalpy, and entropy changes. In no case have the investigations been extended over all the halide systems, and most often the enthalpy values have been found from studies of stability constants at different temperatures. For complicated systems as these such a method can give quite erroneous enthalpy values.¹⁴ To obtain accurate values of the thermodynamic functions, the best method is a potentiometric determination of the stability constants, followed by a direct calorimetric investigation to find the enthalpy changes.

The stability constants used in the present work are mainly those determined by Leden,¹⁵ later on verified by other authors.^{7-9,16} From these 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 heats of reaction were made using a reaction calorimeter and a titration procedure described earlier.¹ The measurements were carried out at a temperature of 25.00°C, and, except for some on the fluoride system with ionic strength 1.00 M, 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 to pH \approx 4.¹⁷

For the calculations of the enthalpy values from the titration data three methods were tried: one graphical, one numerical (solution of equation systems), and one least-squares method using a high speed digital computer. The entropy changes are then obtained from eqn. (2).

CALCULATIONS

The methods of calculation are developed from the equations elaborated by Leden¹⁵ and Fronæus.^{18,19} In this paper only symbols and a short summary are given.

The following symbols and equations have to be introduced:

- I = the ionic strength
- C_M, C_A = » total concentrations of metal ion and ligand
- $[M], [A]$ = » actual » » free metal ion and ligand
- $[MA_j]$ = » » » » the j :th mononuclear complex
- R_x = » resistance of the thermistor (in ohms)
- ΔR_x = » change in resistance at each addition (in ohms; $\Delta R_x < 0$ if heat is evolved)
- Q_x = the corresponding heat change
- $Q_{dil.}$ = » heat of dilution
- $Q_{corr.}$ = » » change corrected for heats of dilution
- v = » volume of titrant added to the calorimeter (in ml)

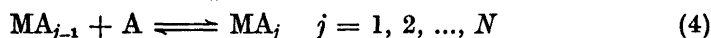
- V = 100.0 + v ; the total volume of the solution in the calorimeter (in ml)
 ϵ_v = the heat equivalent of the calorimeter system at a total volume of V ml (in cal.ohm⁻¹)
 Δh_v = $-\frac{1000}{C_M V} \sum_v Q_{\text{corr.}}$; the total molar enthalpy change after the addition of v ml titrant (in cal.mole⁻¹)
 ΔG_j° = the j :th stepwise free energy change in the standard state (in cal.mole⁻¹)
 ΔH_j° = the j :th stepwise enthalpy change in the standard state (in cal.mole⁻¹)
 ΔS_j° = the j :th stepwise entropy change in the standard state (in cal.mole⁻¹ degree⁻¹)
 β_j = the stability constant of the j :th mononuclear complex
 K_j = the j :th stepwise stability constant

$$\beta_j = \prod_{k=1}^j K_k \quad (3)$$

- \bar{n} = $(C_A - [A])/C_M$; the average bound ligand number per central ion
 α_j = $[MA_j]/C_M$; degree of formation for the j :th complex.

All concentrations are given in mole. l⁻¹ and all heat quantities in thermochemical calories defined by 1 cal. = 4.1840 abs. joules.

If only mononuclear complexes MA_1, MA_2, \dots, MA_N are formed, we obtain for the j :th stepwise reaction the equilibrium:



For this equilibrium the stability constant K_j is defined by:

$$K_j = \frac{[MA_j]}{[MA_{j-1}][A]} \quad (5)$$

The total molar enthalpy change, Δh_v , for a stepwise complex reaction depends on the enthalpy changes for the reaction steps and the amounts of species formed according to the relation:

$$\Delta h_v = \sum_{j=1}^N \sum_{k=1}^j \alpha_j \Delta H_k^\circ \quad (6)$$

which can be transformed into:

$$\Delta h_v = \frac{1}{1 + \sum_{j=1}^N \beta_j [A]^j} \sum_{j=1}^N \sum_{k=1}^j \beta_j [A]^j \Delta H_k^\circ \quad (7)$$

The function $\gamma_1([A])$ defined as:

$$\gamma_1([A]) = \frac{\Delta h_v (1 + \sum_{j=1}^N \beta_j [A]^j)}{[A]} \quad (8)$$

can be calculated from known stability constants, and respective values of experimental data and concentration of free ligand. After simplification, $\gamma_1([A])$ can be written as a polynomial function of $[A]$:

$$\gamma_1([A]) = \sum_{j=1}^N \sum_{k=1}^j \beta_j [A]^{j-1} \Delta H_k^\circ \quad (9)$$

which, by extrapolation to $[A] = 0$, will give:

$$\lim_{[A] \rightarrow 0} \gamma_1([A]) = \beta_1 \Delta H_1^\circ \quad (10)$$

In the general case we obtain:

$$\gamma_n([A]) = \{\gamma_{n-1}([A]) - \lim_{[A] \rightarrow 0} \gamma_{n-1}([A])\} / [A] = \sum_{j=1}^N \sum_{k=1}^j \beta_j [A]^{j-n} \Delta H_k^\circ \quad (11)$$

and by extrapolation to $[A] = 0$:

$$\lim_{[A] \rightarrow 0} \gamma_n([A]) = \beta_n \sum_{k=1}^N \Delta H_k^\circ \quad (12)$$

For each system the function Δh_v is calculated from values of C_M , V , and $Q_{\text{corr.}}$. The composition of the solutions after each addition is determined from β_j , C_M and C_A . By use of a number of equations of type (6) it is now possible to compute the enthalpy changes, but for complicated systems the solution of these equations is very time consuming. Instead of this a graphical method can be used. The functions $\gamma_n([A])$ are plotted *versus* $[A]$ and from the extrapolation to $[A] = 0$, the enthalpy changes can be calculated by eqn. (12). To check the values from the graphical method a least-squares program "Letagrop Kalle" developed by Sillén *et al.*^{20,21} for a high speed computer was used. This is a program in the "Letagrop" series, specially designed for calorimetric titration data.

In this program the error square sum U , where:

$$U = \sum_i w_i (Q_{i, \text{corr.}} - Q_{i, \text{corr., calc.}})^2 \quad (13)$$

was minimized. The weight w_i is 1 in these calculations. The input data were the corresponding values of $Q_{\text{corr.}}$ and v , the stability constants β_j , and values of C_M and C_A for the primary solutions. Values of $\sum_{k=1}^j \Delta H_k^\circ$ must also be given, but, as the system is linear, any guess will do. The program will give values of $\sum_{k=1}^i \Delta H_k^\circ$ with their corresponding standard deviations. The standard deviation in the $Q_{\text{corr.}}$ -values is also given.

As seen from eqn. (7), Δh_v is a function of $[A]$. When plotted *versus* \bar{n} (also a function of $[A]$) Δh_v is independent of C_M , if only mononuclear complexes exist (see Fig. 1). If polynuclear complexes are formed, the Δh_v -function depends on C_M .

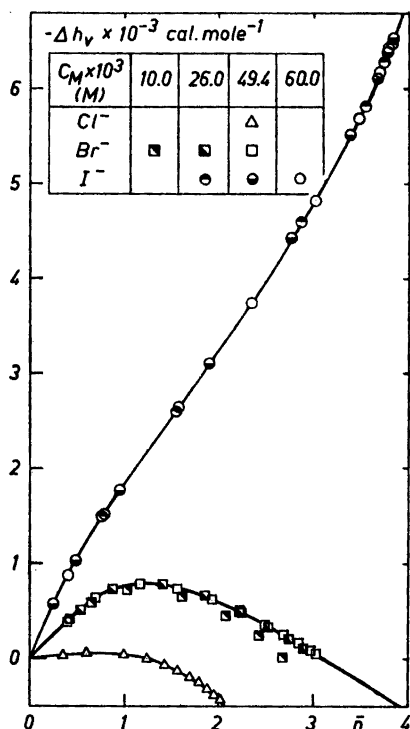


Fig. 1. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the cadmium chloride, bromide, and iodide systems at different central ion concentrations.

EXPERIMENTAL

Chemicals

All chemicals were, if not otherwise stated, of analytical grade and used without further purification.

Cadmium perchlorate was prepared by dissolving cadmium carbonate (Merck, *p.a.*) in an excess of ca. 70 % perchloric acid (Baker Analyzed, *p.a.*), and then evaporated to dryness. A 3.000 M stock solution was prepared by weighing the salt, and analysed by titration with EDTA (Merck, *p.a.*) using Erio-T as indicator. Perchloric acid was added to the stock solution until $pH \approx 2$ to avoid hydrolysis of the Cd(II) ion.¹⁷

Sodium perchlorate was prepared by almost neutralizing ca. 70 % perchloric acid with sodium carbonate (Merck, *p.a.*), boiling off CO_2 , and finally completing the neutralization by sodium hydroxide (*p.a.*). The solution was filtered and then evaporated to saturation. The neutral anhydrous salt crystallized out after cooling to $110^\circ C$. Tests showed no Cl^- or other impurities in the salt. Solutions were prepared by weighing the dried salt. The concentration of some of the solutions were checked by a cation exchange procedure, and no deviation from the calculated values was found.

The ligand solutions of sodium fluoride, chloride, bromide, and iodide were prepared from the dried salts (Baker Analyzed, *p.a.*). Except for the fluoride, the solutions were analysed by titrations with silver nitrate, using $K_2Cr_2O_7$ as indicator. For the chloride solution the result was verified by a gravimetric determination of AgCl.

For the preparation of solutions and the performance of titrations only tested volumetric flasks, burettes, and pipettes were used.

Apparatus

The calorimeter used was an isothermal-jacket titration calorimeter described in an earlier paper.¹ This calorimeter is equipped with a device for the successive addition of known, varying amounts of a titrant. By the use of built-in cooling and heating devices it can be brought back to the standard reference temperature after each addition. The temperature is measured by the use of a thermistor, which gives a sensitivity of 5×10^{-6} degrees, corresponding to a measuring accuracy of better than ± 0.02 cal. The system is electrically calibrated, and the time of equilibration for the system is less than 3 min.

Procedure

The measurements of the reaction heats at the formation of complexes were performed by titration series on a calorimeter solution, S, with up to 25 ml of a titration solution, T. The compositions of the solutions S and T were:



or for some of the measurements on the Cd-F system:



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

The dilution heats of the ligands were determined with similar titration series without cadmium perchlorate (see Table 2). For the central ion, however, no effect was found at dilution from $C_M = 0.060$ to $C_M = 0.001$ in 3 M NaClO₄, and it was assumed that the dilution heats of the various complexes can also be neglected.

For the measurements, the calorimeter was filled with 100.0 ml of a solution S and assembled. A known quantity, varying from 0.5 to 5 ml, of a solution T was then introduced from an all glass syringe into the pipette, in its lower position. The system was equilibrated, and after the initial period, the pipette, now in the upper position, was emptied — the reaction period — with a reproducibility of better than ± 0.002 ml. The pipette was then closed and submerged and the final period started. During the initial

Table 2. The dilution heats for 2.01 ml 3 M NaX added to a homogeneous mixture of 100 ml 3 M NaClO₄ and $v-2$ ml 3 M NaX. $\text{X}^- = \text{Cl}^-, \text{Br}^-$ and I^- . The values of Q_{dil} are averages of two or three series.

v (ml)	$[\text{X}^-]$ (mM)	Q_{dil} (cal)		
		Cl^-	Br^-	I^-
2.01	59.2	-0.200	0.213	-0.040
4.02	115.8	-0.186	0.204	-0.037
6.03	170.4	-0.175	0.202	-0.029
8.04	222.5	-0.165	0.191	-0.026
10.05	273.8	-0.157	0.187	-0.014
12.05	323	-0.151	0.191	-0.015
14.06	370	-0.144	0.179	-0.004
16.07	416	-0.139	0.178	-0.008
18.08	459	-0.135	0.181	-0.009
20.09	502	-0.131	0.171	—

and final periods corresponding values of temperature and time were obtained by measuring the time for a 0.2Ω change in resistance of the thermistor using a balanced bridge. For these small temperature differences a linear dependence of resistance *versus* time during the initial and final periods is found. The change in resistance, ΔR_x , for the various reactions is then obtained by extrapolation of the lines of resistance *versus* time for the initial and final periods, and taken as the difference in the values of R_x at a time t_m , where $t_m = t + 15$ sec is found experimentally. t is the time when the pipette is opened. When the temperature changes were so small as in this investigation, the resistance of the thermistor could be put inversely proportional to the temperature without any significant error. Thus $\Delta T = \text{const.} \times \Delta R_x$. The heat equivalent ε_v of the various systems was determined by electrical calibrations, performed at different values of V . The average values established a linear relation between the heat equivalent of the systems and the total amount of solution T added. For further details see Ref. 1.

By use of known values of the stability constants taken from the literature¹⁵ and the concentrations and the amounts of the solutions S and T, the composition of the liquid phase could be calculated after each addition. The enthalpy change could thus be referred to defined initial and final states.

Standard state

The thermodynamic standard state for the solute species M, A, and MA_i in this study is a hypothetically ideal one molar solution with a neutral salt to ionic strength 3.00 M. (Except for some measurements of the fluoride system with ionic strength 1.00 M). The zero superscript when used with ΔG , ΔH , and ΔS pertains to the standard changes in these quantities referred to this standard state. The activity coefficients of the infinite diluted species M, A, and MA_i in this medium are by definition equal to unity and it is assumed that they do not diverge appreciably from this value in the concentration ranges used. This means that there are no dilution heats from the central ion (proved by experiments) and the complex species during the titration. For the ligand ion, however, the medium change from solution T to S is large during the titration in spite of the constant ionic strength, and we get a ligand dilution heat, depending on the composition of solution T. Moreover, this heat is a function of the final ligand concentration in solution S (see Table 2).

In complex chemistry the use of a medium with a high concentration of neutral salt is a generally accepted method to get constant activity coefficients of solute and solvent over a range of varying composition of the solution. The result of dilution of the halide solutions would indicate a change in the activity coefficients of the ligands in the S solutions during the titration. However, this change is so slight, that it is of no importance for the investigation (proved by experiments).

MEASUREMENTS AND RESULTS

From the electrical calibrations¹ a linear dependence of the heat equivalent on total amount of titrant added was found, closest fit being obtained by use of the method of least-squares, giving the eqn.:

$$-\varepsilon_v = 2.076 + 0.0192 v$$

This function is valid for all the systems investigated with the exception of the fluoride system in $I = 1.00$. The accuracy is better than 5×10^{-3} cal. ohm⁻¹ in the range $0 < v < 25$.

The cadmium(II) fluoride system. This is much weaker than the others here investigated, and in solutions with ionic strength 3.00 M only one complex is formed. For that reason additional measurements have been done in a

solution of $I = 1.00$, in which medium two complexes have been reported.^a The compositions of the solutions S and T are for the measurements at $I = 3.00$:

$$S_1 \begin{cases} C_{Cd(ClO_4)_2} = 0.0600 \\ C_{NaClO_4} = 2.820 \end{cases} \quad T_1 \begin{cases} C_{NaF} = 0.200^b \\ C_{NaClO_4} = 2.800 \end{cases}$$

The heats of dilution were measured by titrations of T_1 into 3.00 M $NaClO_4$. Corresponding values of v , $[F^-]$, Q_x , $Q_{dil.}$, and $Q_{corr.}$ are given in Table 3.

Table 3. The heats of reaction and dilution for two titrations of the F^- -system at ionic strength 3.00 M. The initial cadmium ion concn. is 0.0600 M.

v (ml)	$[F^-]$ (mM)	Q_x (cal)	$Q_{dil.}$ (cal)	$Q_{corr.}$ (cal)
5.02	7.95	-0.097	(0.019)	-0.157
10.05	15.4	-0.111	0.056	-0.167
5.02	7.95	-0.112	0.059	-0.171
10.05	15.4	-0.109	0.065	-0.174
Average values :		-0.107	0.060	-0.167

For the measurements at $I = 1.00$, S and T had the following compositions:

$$S_2 \begin{cases} C_{Cd(ClO_4)_2} = 0.0600 \\ C_{NaClO_4} = 0.820 \end{cases} \quad T_2 \begin{cases} C_{NaF} = 1.00 \end{cases}$$

With these solutions the free ligand concentration was not high enough at the end of the titrations to give information on the second complex. The composition was then changed so that the solution S held the ligand and T the metal:

$$S_3 \begin{cases} C_{NaF} = 0.500 \\ C_{NaClO_4} = 0.500 \end{cases} \quad T_3 \begin{cases} C_{Cd(ClO_4)_2} = 0.0600 \\ C_{NaClO_4} = 0.820 \end{cases}$$

The heats of dilution of the ligand were determined by titrations of T_2 into 1.00 M $NaClO_4$, and 1.00 M $NaClO_4$ into S_3 . No corrections were made for the dilution of the central ion and the complex species. For the result see Table 4, where corresponding values of v , $[F^-]$, Q_x , $Q_{dil.}$, and $Q_{corr.}$ are given.

The cadmium(II) chloride system. In the medium and concentration range used, three mononuclear complexes are formed. The compositions of the solutions S and T were:

$$S_4 \begin{cases} C_{Cd(ClO_4)_2} = 0.0494 \\ C_{NaClO_4} = 2.850 \end{cases} \quad T_4 \begin{cases} C_{NaCl} = 3.000 \end{cases}$$

^a From a polarographic study of the Cd-F system by Mesarić and Hume,²² it is assumed that only one complex exists in $I = 2.00$, and the given value of β_1 is 6.4. This value, however, does not agree with the result from this calorimetric investigation, and as the uncertainty in the polarographic study is great, the constants of Leden¹⁵ have been chosen.

^b This was the highest possible concentration of NaF in the medium used.

Table 4. The heats of reaction and dilution for titration of the F^- -system at ionic strength 1.00 M. The values of Q_x and $Q_{dil.}$ are averages of two or three series. Titrations of type I are performed with ligand solution into central ion solution, and of type II with central ion into ligand. The initial cadmium ion concn. is 0.0600 M.

Titration type	v (ml)	$[F^-]$ (mM)	Q_x (cal)	$Q_{dil.}$ (cal)	$Q_{corr.}$ (cal)	$\sum Q_{corr.}$ (cal)
I	5.02	41.2	-1.402	-0.552	-0.850	-0.850
	10.05	79.4	-1.075	-0.536	-0.539	-1.389
	15.07	115.0	-1.003	-0.519	-0.484	-1.873
	20.09	148.0	-0.872	-0.490	-0.382	-2.255
II	5.02	473	-0.354	-0.153	-0.201	-0.201
	10.05	449	-0.337	-0.143	-0.194	-0.395

The heats of dilution were measured by titrations of solution T_4 into 3.00 M $NaClO_4$. Corresponding values of v , $[X^-]$, and $Q_{dil.}$ are collected in Table 2 and of v and $Q_{corr.}$ in Table 5. In Fig. 1 the Δh_v -function is plotted versus \bar{n} . When the correction:

$$Q_x - Q_{dil.} = Q_{corr.} \quad (14)$$

is made, regard must be taken to the complex formation, and $Q_{dil.}$ is thus calculated for the dilution of the ligand solution from 3.000 M to the actual concentration of the free ligand in the reaction solution.

The cadmium(II) bromide system. Four mononuclear bromide complexes are reported in the medium used here. In order to check any formation of

Table 5. The reaction heats, corrected for dilution, obtained at the titrations of the Cl^- , Br^- , and I^- systems. The values of $\sum Q_{corr.}$ are averages of two or three series. C_M is the initial cadmium ion concn. in the S solutions.

Ligand	$\sum Q_{corr.}$ (cal)						
	Cl^-	Br^-			I^-		
$C_M(M)$	0.0494	0.0100	0.0260	0.0494	0.0260	0.0494	0.0600
v (ml)							
0.502		0.402				2.841	
1.005	0.181	0.583	1.276	1.929	3.984	5.127	5.258
2.009	0.266	0.719	1.806	3.101	6.733	8.720	9.117
4.018	0.188	0.658	1.959	3.903	12.037	15.339	15.794
6.027	-0.032	0.464	1.670	3.698	15.129	21.897	22.506
8.036	-0.309	0.267	1.256	3.110	16.257	27.239	28.962
10.045	-0.622	0.080	0.868	2.412	16.727	30.163	34.145
12.054	-0.938		0.536	1.803		31.526	37.058
14.063	-1.254		0.277	1.260		32.254	38.482
16.072	-1.570			0.815			39.245
18.081	-1.880			0.458			
20.090	-2.175			0.310			

polynuclear complexes, measurements were made at different concentrations of the central ion, but no effect due to this could be detected. The compositions of the solutions S and T were:

$$S_{5-7} \begin{cases} C_{\text{Cd}(\text{ClO}_4)_2} = 0.0100, 0.0260, 0.0494 \\ C_{\text{NaClO}_4} = 2.970, 2.922, 2.850 \end{cases} \quad T_{5-7} \begin{cases} C_{\text{NaBr}} = 3.000 \end{cases}$$

The dilution heats were determined as above. For the results see Tables 2 and 5. In Fig. 1 the Δh_v -function for different C_M is plotted *versus* \bar{n} . No change in Δh_v , which would indicate polynuclear species, can be found at varying C_M . The influence of the stability constants on the enthalpy changes has been examined by using different sets of constants (see Table 6).

Table 6. Enthalpy values for the bromide and iodide systems using different sets of β_j -values.

The Br ⁻ -system			The I ⁻ -system		
β_j	A	$\sigma Q_{\text{corr.}}$ (cal)	β_j	A	$\sigma Q_{\text{corr.}}$ (cal)
54	1.002 ± 0.003	0.01690	120	2.304 ± 0.021	0.05173
250	1.352 ± 0.012		700	1.171 ± 0.334	
1800	-0.208 ± 0.016		1 × 10 ⁵	3.735 ± 0.070	
5800	-0.419 ± 0.020		3 × 10 ⁵	7.063 ± 0.025	
57	0.976 ± 0.003	0.01719	121	2.258 ± 0.007	0.01806
220	1.541 ± 0.014		600	2.453 ± 0.114	
2100	-0.183 ± 0.012		8.2 × 10 ⁴	3.181 ± 0.024	
5000	-0.487 ± 0.019		3.3 × 10 ⁵	6.994 ± 0.006	
60	0.953 ± 0.003	0.01773	121	2.244 ± 0.009	0.02259
190	1.784 ± 0.017		500	2.962 ± 0.208	
2400	-0.149 ± 0.011		8.0 × 10 ⁴	2.946 ± 0.040	
4400	-0.574 ± 0.023		3.5 × 10 ⁵	6.975 ± 0.010	

$$A: - \left(\sum_{k=1}^j \Delta H_k^\circ \pm \sigma \sum_{k=1}^j \Delta H_k^\circ \right) 10^{-3} \text{ cal. mole}^{-1}.$$

The cadmium(II) iodide system. This system also forms four complexes in the medium used. Measurements were made at different concentrations of the central ion, but no effect due to formation of any polynuclear complexes could be found. The compositions of solutions S and T were:

$$S_{8-10} \begin{cases} C_{\text{Cd}(\text{ClO}_4)_2} = 0.0260, 0.0494, 0.0600 \\ C_{\text{NaClO}_4} = 2.922, 2.850, 2.820 \end{cases} \quad T_{8-10} \begin{cases} C_{\text{NaI}} = 3.000 \end{cases}$$

The dilution heats were determined as above. For the results see Tables 2 and 5 and Fig. 1.

The amounts of the second complex species in this system are so small during the whole titration, that the accuracy for this step is very low. To get the best possible result, different sets of stability constants have been

used during the calculations to minimize the error square sum (see Table 6). In this way it is possible not only to get the enthalpies, but also to check and refine the stability constants by calorimetric measurements.

From the experimental values collected in Tables 3 to 5, the enthalpy changes for the stepwise reactions:



can be calculated using the methods described.

These values, together with corresponding values of the free energy and the entropy changes, have been collected in Table 8, and can be compared with earlier published data found in Table 1.

Table 7. The differences ($Q_{\text{corr.}} - Q_{\text{corr., calc}}$) for the Cl^- , Br^- , and I^- systems. For every system and concentration one representative series is taken.

Ligand $C_M(\text{M})$		$(Q_{\text{corr.}} - Q_{\text{corr., calc}})$ (cal)						
		Cl^-	Br^-			I^-		
v (ml)		0.0494	0.0100	0.0260	0.0494	0.0260	0.0494	0.0600
0.502			-0.009				0.052	
1.005	-0.016		0.013	0.017	-0.040	0.166	-0.018	-0.006
2.009	-0.005		0.019	0.025	-0.008	0.003	0.054	-0.029
4.018	0.037		0.011	-0.012	0.007	0.021	0.085	0.026
6.027	0.016		0.028	-0.032	-0.005	-0.096	0.041	0.013
8.036	-0.029		0.016	-0.001	-0.018	-0.043	-0.039	-0.032
10.045	-0.030		0.027	-0.003	-0.012	-0.020	-0.057	0.005
12.054	-0.032			0.011	-0.008		-0.013	0.002
14.063	-0.009			0.005	-0.014		0.026	-0.008
16.072	0.021				-0.030			-0.019
18.081	0.013				-0.035			
20.090	0.026				0.005			

Accuracy of the results. The error in $Q_{\text{corr.}}$ depends on the two measured values Q_x and $Q_{\text{dil.}}$, which are reproduced to better than ± 0.02 cal (see above). In Table 7 are given the values of the difference ($Q_{\text{corr.}} - Q_{\text{corr., calc.}}$) for the chloride, bromide, and iodide systems. No systematic errors can be found. (For every system one representative series is chosen.) The magnitude of the differences ($Q_{\text{corr.}} - Q_{\text{corr., calc.}}$) is that expected from the accuracy of the calorimeter. The error in the enthalpy changes, however, depends also on the accuracy of the stability constants, but calculations using different sets of constants give, with the exception of the iodide system, step two, only small variations in the ΔH_j° -values (see Table 6). From the given error in the free energy change and the standard deviation in the enthalpy term the uncertainty in the corresponding entropy term has been estimated.

Table 8. The stability constants used and the computed values of free energy, enthalpy, and entropy changes for the stepwise reactions of the four cadmium 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. Ionic strength 3.00 M if not otherwise stated.

Ligand	F^-	F^- ($I = 1$)	Cl^-	Br^-	I^-
β_j	$j = 1$	3.7 ± 0.1	2.9 ± 0.2	38.5 ± 1	57 ± 2
	2	—	3.4 ± 0.2	170 ± 10	220 ± 20
	3	—	—	260 ± 10	2100 ± 200
	4	—	—	—	5000 ± 500
$-\Delta G_j^\circ \times 10^{-3}$ (cal. mole $^{-1}$)	1	0.78 ± 0.02	0.63 ± 0.04	2.16 ± 0.02	2.40 ± 0.02
	2	—	0.11 ± 0.07	0.88 ± 0.05	0.80 ± 0.08
	3	—	—	0.25 ± 0.06	1.34 ± 0.11
	4	—	—	—	0.51 ± 0.12
$-\Delta H_j^\circ \times 10^{-3}$ (cal. mole $^{-1}$)	1	-1.02 ± 0.05	-1.23 ± 0.05	0.10 ± 0.01	0.98 ± 0.01
	2	—	0.72 ± 0.11	-0.02 ± 0.02	0.57 ± 0.02
	3	—	—	-1.85 ± 0.05	-1.72 ± 0.03
	4	—	—	—	-0.30 ± 0.03
ΔS_j° (cal. mole $^{-1}$ degree $^{-1}$)	1	6.0 ± 0.2	6.2 ± 0.3	6.9 ± 0.1	4.7 ± 0.1
	2	—	-2.0 ± 0.6	3.0 ± 0.2	0.8 ± 0.3
	3	—	—	7.0 ± 0.3	10.2 ± 0.5
	4	—	—	—	2.7 ± 0.5

^a The sum is better determined for these two steps.

DISCUSSION

If the values of enthalpy changes determined in this investigation are compared with earlier results (see Tables 1 and 8), many discrepancies will be found. However, these may partly be due to different ionic strength and temperature, partly to inappropriate methods used in the past. Some of the values, *e.g.* those reported by Shchukarev *et al.*⁹ for the chloride system, and Becker *et al.*¹³ for the iodide system, are of the same order as those found in this study.

The complexes investigated are built up from one central ion and a series of nearly related ligands. This was assumed to give a continuous variation not only in the free energy change as found earlier, but also in the enthalpy and entropy terms between the systems. The investigation confirmed this, and furthermore it turned out, that the increase in stability, when going from F^- to I^- , is determined by the variation in the enthalpy term, which is greater than and opposed to that in the entropy term (see Table 8 and Fig. 2). There seems to be a relation between the enthalpy change and the degree of covalency of the bond.

The variations in the enthalpy and entropy terms of the stepwise reactions, going from lower to higher steps, are found to have a similar trend for the chloride, bromide and iodide systems, for which the stability of the third step to a great part is governed by entropy factors, while the enthalpy term is more important for the fourth (see Table 8 and Figs. 3–5).

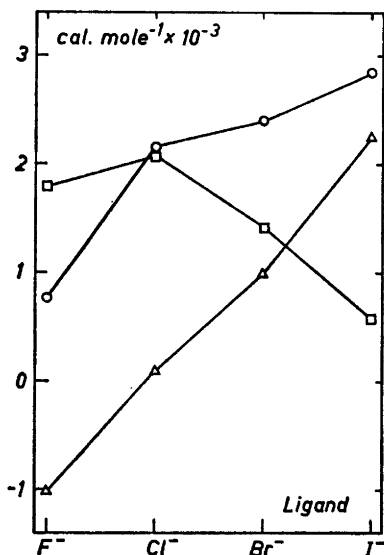


Fig. 2. The values of $-\Delta G_1^\circ$ (O), $-\Delta H_1^\circ$ (Δ), and $T\Delta S_1^\circ$ (\square) for the four cadmium halide systems.

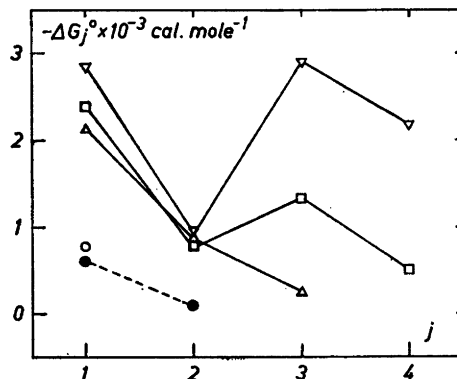


Fig. 3. The values of $-\Delta G_j^\circ$ for the four cadmium halide systems. F^- O, F^- ($I = 1$) \bullet , Cl^- Δ , Br^- \square , and I^- ∇ .

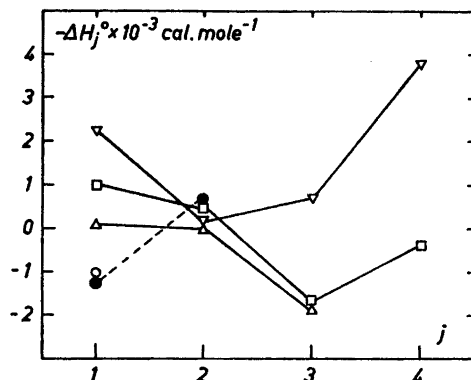


Fig. 4. The values of $-\Delta H_j^0$ for the four cadmium halide systems. $\text{F}^- \text{O}$, $\text{F}^- (I = 1)$ ●, Cl^- △, Br^- □, and I^- ▽.

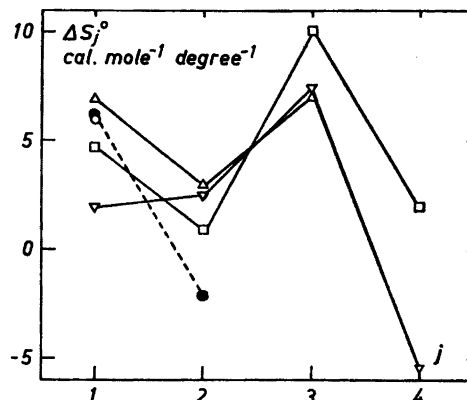


Fig. 5. The values of ΔS_j^0 for the four cadmium halide systems. $\text{F}^- \text{O}$, $\text{F}^- (I = 1)$ ●, Cl^- △, Br^- □, and I^- ▽.

The stability constants can in some cases be calculated or refined by calorimetric data, either with measurements at different C_M using a graphic method,¹⁸ or with a least-squares method using a high speed computer.^{20,21} From the measurements at varying C_M no effect of polynuclear species can be found. For the Cd-Br system Δh_v -values for the lowest cadmium concentration, $C_M = 0.010$, diverge from the others, but this is probably due to the greater uncertainty in these measurements.

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