

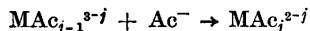
Thermochemical Studies on Metal Complexes

V. Free Energy, Enthalpy, and Entropy Changes for Stepwise Formation of Some Metal(II) Acetate Complexes in Aqueous Solution

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The enthalpy changes for the stepwise reactions:



where M^{2+} is the copper(II), zinc(II), cadmium(II), or lead(II) ion, have been determined by a direct calorimetric titration procedure. From these enthalpy changes and the changes in free energy, computed from corresponding 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.

In the acetate systems studied nearly all the species are formed by entropy stabilized endothermic reactions. The difference in stability of the systems, especially for the first step, can be assigned to the enthalpy term, while the entropy term for each step, respectively, is of about the same magnitude for all the four systems.

In previous investigations^{1,2} the changes in free energy, enthalpy, and entropy for the stepwise formation of some cadmium(II) complexes with different ligands have been determined. For those systems the stabilizing term in the relation:

$$\Delta G_j^\circ = \Delta H_j^\circ - T\Delta S_j^\circ \quad (1)$$

was in general the enthalpy one, and the variation in this term was also the cause of the increasing stability from the fluoride to the iodide system, and of the extreme stability of the cyanide system. An interesting problem would be to study a series of complexes with different central ions of the same charge. Therefore, in this investigation, the thermodynamic properties, ΔG° , ΔH° , and ΔS° , have been studied for some complex systems, in which the central ion has been varied. The metal ions chosen were copper(II), zinc(II), cadmium(II), and lead(II). The ligand was the acetate ion, which gives complexes within a suitable range of stability.

The systems investigated now have been studied previously, among others by Tanaka *et al.*^{3,4} using a polarographic method. They determined the stability constants at 15°, 25°, and 35°C at an ionic strength of 0.2 M. From these values the enthalpy changes can be determined with only low reliability. For the copper(II) acetate system $-\Delta H_1^\circ$ was calculated to about -5×10^3 (cal mole⁻¹) and for the other acetates to between $+2$ and $+4 \times 10^3$ (cal mole⁻¹). Very few calorimetric investigations of acetate systems have been performed. Pocock and Rossotti⁵ have studied the copper(II) system and found $-\Delta H_1^\circ = -1.01 \times 10^3$ (cal mole⁻¹) and Grenthe has made a systematic study of the lanthanoide systems, and found them to be entropy stabilized.⁶

The stability constants used in the present investigation were either determined earlier at this department, as for copper(II),⁷ zinc(II),⁸ and cadmium(II),⁹ or taken from the literature, as for lead(II).¹⁰ From these constants the changes in free energy of the reactions and the concentrations of the various complex species in the solutions have been calculated. The enthalpy changes were obtained using a reaction calorimeter and a titration method described previously.¹¹ The measurements were carried out at a temperature of 25.00°C in an aqueous sodium perchlorate medium of ionic strength 3.00 M. The hydrolysis of the metal ions was suppressed by an accurately balanced excess of perchloric acid.

The calculations of the enthalpy values from the experimental data and a list of symbols and equations used have been described in an earlier paper.¹ Two methods were tried: one graphical and one least squares procedure. The latter was developed by Sillén and Ingri,^{12,13} and uses a high speed digital computer. The entropy changes are then obtained from eqn. (1).

EXPERIMENTAL

Chemicals

Copper(II) perchlorate was prepared by dissolving copper(II) oxide (Baker Analyzed, *p.a.*) in an excess of *ca.* 70% perchloric acid (Baker Analyzed, *p.a.*). The solution was evaporated with the acid until no chloride ions could be detected. After further evaporation to dryness, the crystals were dissolved in water and the solution filtered. The copper concentration in the solutions used was determined by electrolysis or by titrations with EDTA using murexid as indicator. To suppress hydrolysis of the copper(II) ion the solutions contained perchloric acid sufficient to maintain the pH at 3.3–4.0.¹⁴

Zinc(II) perchlorate was prepared by dissolving zinc(II) oxide (Baker Analyzed, *p.a.*) in an excess of *ca.* 70% perchloric acid (Baker Analyzed, *p.a.*), followed by evaporation. The zinc concentration in the solutions used was determined by EDTA using Erio-T as indicator. To avoid hydrolysis the solutions were acidified to pH 4.0–4.5.^{15,16}

Cadmium(II) perchlorate was prepared according to Ref. 1, and the solutions analysed by EDTA using Erio-T as indicator. The pH was 4–5 in the solutions used, to suppress hydrolysis.¹⁷

Lead(II) perchlorate was prepared by dissolving lead(II) oxide (Baker Analyzed, *p.a.*) as described by Olin.¹⁸ The solutions used were analysed by EDTA using Erio-T as indicator, and to avoid hydrolysis the pH was maintained at 3.5–4.0.¹⁸

Sodium perchlorate was prepared according to Ref. 1, and the dried salt checked by a cation exchange procedure. No impurities as chloride or chlorate ions could be found but it contained a protolytic system with a total buffer effect of less than 4×10^{-5} moles per mole of sodium perchlorate, which was neglected. The ionic medium was maintained in all solutions used by adding weighed amounts of this salt.

The acetate buffers were prepared from crystallized sodium acetate, $\text{NaAc}\cdot 3\text{H}_2\text{O}$, (Merck, *p.a.*) and 99.5 % acetic acid (Merck, *p.a.*). The solutions were analysed for acetic acid and acetate by potentiometric titrations with sodium hydroxide and perchloric acid, respectively.

Procedure

The same calorimetric and titration procedures were used as described in a previous paper.¹¹ This calorimeter was equipped with a device for the successive addition of known amounts, 1–5 ml portions up to a total of 30 ml, of a titrant, T, into a calorimeter solution, S, initial volume 100.0 ml. The compositions of the solutions S and T were:

$$S \begin{cases} C_M & M M(\text{ClO}_4)_2 \\ (3.000 - 3 C_M) M \text{NaClO}_4 \end{cases} \quad T \begin{cases} C_A & M \text{NaAc} \\ C_{\text{HA}} & M \text{HAc} \\ (3.000 - C_A) & M \text{NaClO}_4 \end{cases}$$

or, for some measurements:

$$S \begin{cases} C_A & M \text{NaAc} \\ C_{\text{HA}} & M \text{HAc} \\ (3.000 - C_A) & M \text{NaClO}_4 \end{cases} \quad T \begin{cases} C_M & M M(\text{ClO}_4)_2 \\ (3.000 - 3 C_M) & M \text{NaClO}_4 \end{cases}$$

In general, at least two series of measurements were carried out with each pair of solutions.

The dilution heats of the ligand solutions were determined at similar titration series but with no metal ions. These heats must involve effects from several reactions, *e.g.* dilution of acetic acid and acetate ions and dissociation of HAc , H_2Ac_2 , and HAc_2^- .¹⁹ It is presumed that all of these reactions take place to the same extent during measurements with and without metal ions. The reaction heats obtained at mixing solutions T and S, are then corrected for the heats obtained at mixing the same amounts of T and S when $C_M = 0$. For the central ions no effect was found upon diluting from $C_M = 0.100$ to $C_M = 0.002$ in 3 M NaClO_4 , 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, is, in this study, a temperature of 25.00°C and 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^{1,11} 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 two relations:

$$-\varepsilon_v = 2.084 + 0.0197 v \quad (2)$$

$$-\varepsilon_v = 2.129 + 0.0198 v \quad (3)$$

Eqn. (2) is valid for the series titrated when a 2 ml pipette was used for the additions; eqn. (3) for the series titrated with a 5 ml pipette. The accuracy is better than $\pm 5 \times 10^{-3}$ cal ohm^{-1} in the range $0 < v < 30$. No differences were observed between systems with various metal ions and buffers.

Dilution heats of ligand solutions. Dilutions of the buffer solutions into 3.000 M NaClO_4 , gave considerable heat effects (see Table 1). When the complex titrations are performed, the conditions are changed compared to the dilution experiments, and it is clear that the correction technique could be the cause of errors. In fact quite different heats are obtained when buffer solutions of ionic strength 3.00 M are diluted into 2.50 M NaClO_4 and 3.00 M NaClO_4 .

Table 1. The dilution heats for the additions of 2.009 ml or 5.023 ml of the ligand solution T into initially 100.0 ml 3.000 M NaClO₄. The values of Q_{dil} are taken from a smoothed curve obtained as an average of several series.

C_A (M)	Q_{dil} (cal)							
	1.000	1.500	1.500	1.500	1.500	1.500	3.000	3.000
C_{HA} (M)	1.000	0.000	0.150	0.500	1.500	3.000	1.000	1.000
C_A/C_{HA}	1	∞	10	3	1	1/2	3	3
v (ml)								
2.009	0.276	-0.170	-0.067	0.063	0.514	1.406	0.204	
4.018	0.266	-0.160	-0.067	0.057	0.499	1.345	0.201	
5.023								0.543
6.027	0.255	-0.155	-0.068	0.051	0.484	1.294	0.199	
8.036	0.245	-0.150	-0.068	0.046	0.468	1.248	0.197	
10.045	0.235	-0.145	-0.069	0.040	0.453	1.208	0.194	0.514
12.054	0.226		-0.069	0.034	0.437	1.171	0.192	
14.063	0.216		-0.070	0.028	0.421	1.137	0.190	
15.068								0.484
16.072	0.206		-0.070	0.023	0.405	1.107	0.188	
18.081	0.197						0.186	
20.09	0.188						0.183	0.455
25.11								0.426

solutions, respectively.¹⁹ The differences in dilution heats for each buffer in the two solutions per 2 ml addition are of the order 0.5 cal. However, so large a concentration difference as 0.5 M in the ionic strength is never reached during the experiments, and for $C_M \leq 0.050$ (M) the effects are negligible for ΔH_1° , and small for ΔH_2° (checked at the measurements of the lead(II) system).

For constant C_M the agreement of the measurements for different buffers is good when hydrolysis can be neglected (see the copper(II) and the lead(II) systems) which would indicate an adequate correction for dilution heats.

The copper(II) acetate system. To study the effect of hydrolysis and dilution heat corrections the calorimetric titrations of this system were performed with different buffers. The copper concentration was also changed during the measurements and the compositions of the solutions S and T were:

$$\begin{array}{l}
 \text{S} \left\{ \begin{array}{l} 0.025, 0.050, 0.100 \text{ M Cu}(\text{ClO}_4)_2 \\ 2.925, 2.850, 2.700 \text{ M NaClO}_4 \end{array} \right. \\
 \text{T} \left\{ \begin{array}{l} 1.000, 1.500, 1.500, 1.500, 1.500, 1.500 \text{ M NaAc} \\ 1.000, 0.000, 0.150, 0.500, 1.500, 3.000 \text{ M HAc} \\ 2.000, 1.500, 1.500, 1.500, 1.500, 1.500 \text{ M NaClO}_4 \end{array} \right.
 \end{array}$$

A systematic variation in reaction heats evolved was obtained with pH of the buffers (see Table 2 and Fig. 1 a). The hydrolysis is suppressed in the two most acidic buffers, as is indicated by the experimental data, and so the enthalpy values are determined in this range. The pH of the S solutions had also to be exactly balanced to avoid neutralisation heats at the first

Table 2. The reaction heats, corrected for dilution, obtained at the titrations of the copper(II) system at various C_M and pH. C_M is the initial copper ion concentration in the S solutions, C_A the acetate ion concentration and C_{HA} the acetic acid concentration in the T solutions.

		$\sum Q_{\text{corr.}}$ (cal)										
C_M (M)		0.025	0.050	0.100	0.050	0.050	0.050	0.050	0.050	0.050	0.050	
C_A (M)		1.000	1.000	1.000	1.500	1.500	1.500	1.500	1.500	1.500	1.500	
C_{HA} (M)		1.000	1.000	1.000	0.000	0.150	0.500	1.500	3.000			
C_A/C_{HA}		1	1	1	∞	10	3	1	1/2			
v (ml)												
2.009		-1.055	-1.042	-1.514	-1.505	-1.749	-1.758	-4.193	-3.255	-2.553	-2.015	-1.928
4.018		-1.753	-1.730	-2.740	-2.731	-3.338	-3.356	-6.889	-5.391	-4.223	-3.457	-3.379
6.027		-2.211	-2.183	-3.689	-3.696	-4.804	-4.809	-8.709	-6.737	-5.280	-4.379	-4.371
8.036		-2.519	-2.480	-4.436	-4.437	-6.100	-6.112	-9.886	-7.496	-5.892	-4.957	-5.036
10.045		-2.708	-2.676	-5.018	-4.999	-7.226	-7.270	-10.696	-7.890	-6.265	-5.312	-5.485
12.054		-2.860	-2.821	-5.446	-5.423	-8.222	-8.264		-8.983	-6.485	-5.547	-5.812
14.063		-2.979	-2.931	-5.773	-5.745	-9.082	-9.082		-8.155	-6.505	-5.673	-6.041
16.072		-3.075	-3.005	-6.029	-5.992	-9.794	-9.867		-8.152	-6.593	-5.761	-6.225
18.081				-6.225	-6.183	-10.409	-10.492					
20.09				-6.386	-6.333	-10.934	-11.017					

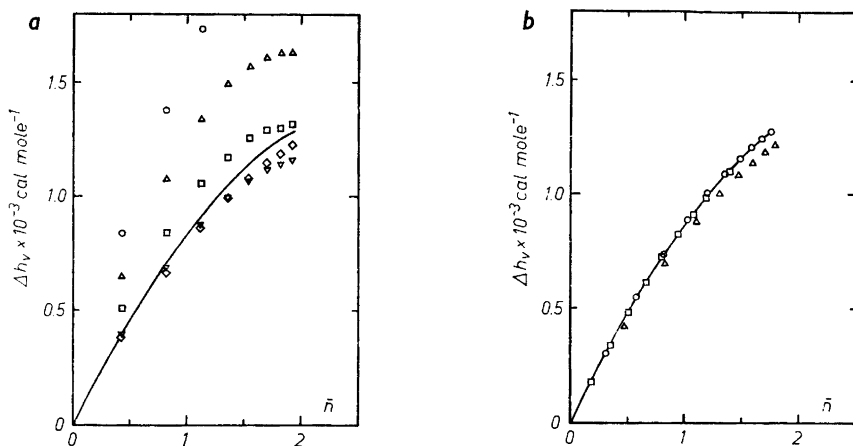
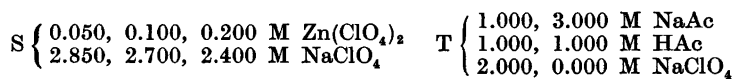


Fig. 1. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the copper acetate system. *a*: at different pH, $C_M = 0.050$. $C_A/C_{HA} = \infty$ (\circ); $C_A/C_{HA} = 10$ (Δ); $C_A/C_{HA} = 3$ (\square); $C_A/C_{HA} = 1$ (∇); $C_A/C_{HA} = 1/2$ (\diamond). *b*: at different central ion concentrations, $C_A = C_{HA} = 1.000$. $C_M = 0.025$ (Δ); $C_M = 0.050$ (\circ); $C_M = 0.100$ (\square).

additions, caused by hydrolysis products. The measurements with various C_M gave no regular variation (see Fig. 1 b).

The experimental data of dilution heats are given in Table 1, and the values of v and $\sum Q_{\text{corr}}$ in Table 2. The Δh_v -functions are plotted versus \bar{n} in Figs. 1 a and 1 b. Experimental points are denoted by various signs and values calculated from determined enthalpy changes by continuous curves. The values of ΔG_j° , ΔH_j° , and ΔS_j° with their estimated errors are collected in Table 8.

The zinc(II) acetate system. Both the buffer composition and the metal ion concentration were varied in the measurements of this system. The solutions S and T contained:



No distinct variations are observed either with pH or C_M (see Fig. 2). This could be expected because the hydrolysis of this system^{15,16} is not as strong as for the copper one and no polynuclear species of zinc acetate have been proved.⁸ The experimental data are collected in Tables 1 and 3 and calculated values of the Δh_v -functions plotted versus \bar{n} in Fig. 2.

Because of the slight tendency of complex formation the concentration of free ligand is not high enough at the end of the ordinary titrations. To obtain information about the third complex the compositions of the solutions were changed and now T contained the metal ion and S the ligand:

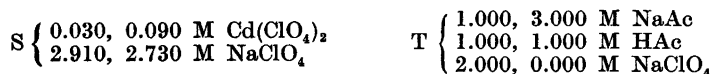


Table 3. The reaction heats, corrected for dilution, obtained at the titrations of the zinc(II) system at various C_M and pH. C_M is the initial zinc ion concentration in the S solutions. C_A and C_{HA} are the acetate ion and acetic acid concentrations, respectively, in the T solutions.

		$\sum Q_{\text{corr.}} \text{ (cal)}$							
C_M (M)	0.050		0.050		0.100		0.200		
C_A (M)	1.000		3.000		3.000		3.000		
C_{HA} (M)	1.000		1.000		1.000		1.000		
C_A/C_{HA}	1		3		3		3		
v (ml)									
2.009	-1.240	-1.214							
2.511			-4.473	-4.454					
4.018	-2.453	-2.444							
5.023			-8.386	-8.357	-13.459	-13.532	-18.369	-18.336	
6.027	-3.635	-3.628							
8.036	-4.761	-4.758							
10.045	-5.872	-5.843	-14.713	-14.702	-24.835	-24.892	-35.668	-35.607	
12.054	-6.924	-6.883							
14.063	-7.923	-7.877							
15.068			-18.896	-18.936	-33.313	-33.399	-50.754	-50.700	
16.072	-8.887	-8.831							
18.081	-9.791	-9.735							
20.09	-10.648	-10.592	-21.709	-21.711	-39.353	-39.437	-62.910	-62.770	
25.11			-23.579	-23.546	-43.609	-43.695	-72.577	-72.345	

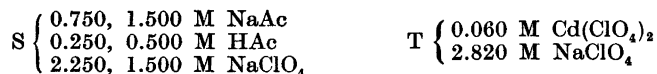
The results are given in Table 4 and the agreement with earlier series can be seen from Fig. 2. The values of ΔG_i° , ΔH_i° , and ΔS_i° with their estimated errors are collected in Table 8.

The cadmium(II) acetate system. In the measurements of this system both the buffer composition and the metal ion concentration have been varied. The solutions S and T contained:



The experimental data are collected in Tables 1 and 5 and the Δh_v -functions are plotted *versus* \bar{n} in Fig. 3. The influence of pH and C_M is small as for the zinc system (see Fig. 3), and both effects can be explained by errors in the correction technique for the dilution heats.

To obtain better information about the third complex, experiments were performed with the solutions changed, as for the zinc system, and the compositions were:



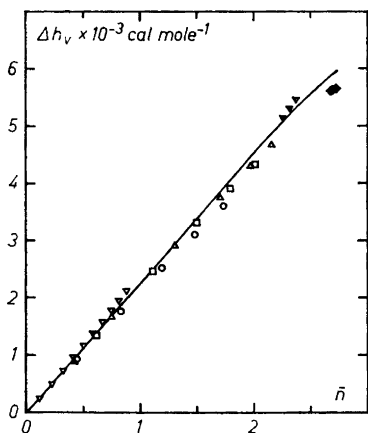


Fig. 2. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the zinc acetate system at different central ion concentrations and pH. $C_A = C_{HA} = 1.000$: $C_M = 0.050$ (∇). $C_A = 3.000$, $C_{HA} = 1.000$; $C_M = 0.050$ (Δ); $C_M = 0.100$ (\square); $C_M = 0.200$ (\circ). Additions of metal ion into ligand solutions, $C_M = 0.200$: $C_A = 0.750$, $C_{HA} = 0.250$ (∇); $C_A = 1.500$, $C_{HA} = 0.500$ (\blacklozenge).

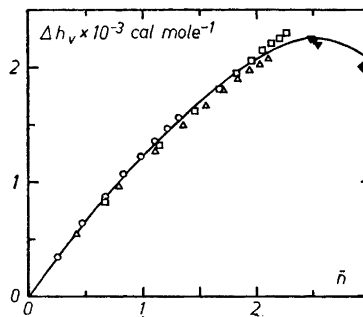


Fig. 3. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the cadmium acetate system at different central ion concentrations and pH. $C_A = C_{HA} = 1000$, $C_M = 0.030$ (\circ). $C_A = 3.000$, $C_{HA} = 1.000$; $C_M = 0.030$ (\square); $C_M = 0.090$ (Δ). Additions of metal ion into ligand solutions, $C_M = 0.060$: $C_A = 0.750$, $C_{HA} = 0.250$ (∇); $C_A = 1.500$, $C_{HA} = 0.500$ (\blacklozenge).

Table 4. The dilution heats and the total corrected reaction heats obtained for the zinc(II) and cadmium(II) systems when the metal ion is added to the ligand solution. C_A and C_{HA} are the acetate ion and the acetic acid concentrations, respectively, in the S solutions. C_M is the metal ion concentration in the T solutions.

	Q_{dil} (cal)		ΣQ_{corr} (cal)			
	C_M (M)		$[Zn^{2+}] = 0.200$		$[Cd^{2+}] = 0.060$	
C_A (M)	0.750	1.500	0.750	1.500	0.750	1.500
C_{HA} (M)	0.250	0.500	0.250	0.500	0.250	0.500
v (ml)						
5.023	0.073	0.127	-5.558	-5.738	-0.658	-0.596
10.045	0.066	0.116	-10.778	-11.433	-1.345	-1.195
15.068	0.056	0.105	-15.686	-17.067	-2.024	-1.813

The results are tabulated in Table 4. In Fig. 3 the Δh_v -values are plotted versus \bar{n} . The values of ΔG_j° , ΔH_j° , and ΔS_j° are given in Table 8 with their estimated errors.

Table 5. The reaction heats, corrected for dilution, obtained at the titrations of the cadmium(II) system at various C_M and pH. C_M is the initial cadmium ion concentration in the S solutions. C_A and C_{HA} are the acetate ion and acetic acid concentrations, respectively, in the T solutions.

		$\sum Q_{\text{corr.}} \text{ (cal)}$				
C_M (M)		0.030		0.030		0.090
C_A (M)		1.000		3.000		3.000
C_{HA} (M)		1.000		1.000		1.000
C_A/C_{HA}		1		3		3
v (ml)		1		3		3
2.009	-1.055	-1.028	-2.471	-2.455	-4.834	-4.880
4.018	-1.933	-1.904	-3.954	-3.918	-8.587	-8.628
6.027	-2.631	-2.621	-4.867	-4.844	-11.383	-11.418
8.036	-3.214	-3.211	-5.425	-5.413	-13.444	-13.486
10.045	-3.675	-3.679	-5.821	-5.855	-14.996	-15.045
12.054	-4.068	-4.074	-6.195	-6.199	-16.130	-16.221
14.063	-4.388	-4.389	-6.466	-6.451	-16.981	-17.119
16.072	-4.678	-4.677	-6.649	-6.656	-17.609	-17.806
18.081			-6.796	-6.820	-18.132	-18.306
20.090			-6.903	-6.971	-18.568	-18.725

The lead(II) acetate system. Even for this system both the buffer composition and the metal ion concentration were varied in the measurements. The solutions S and T contained:

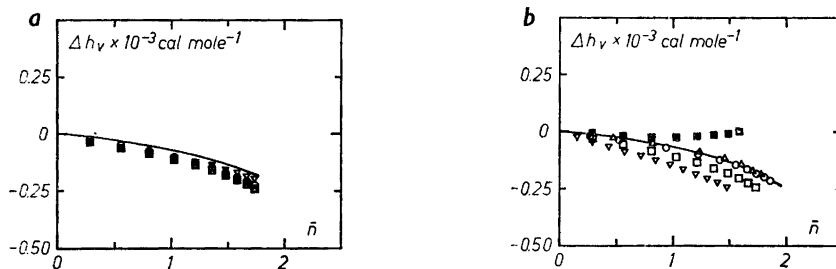
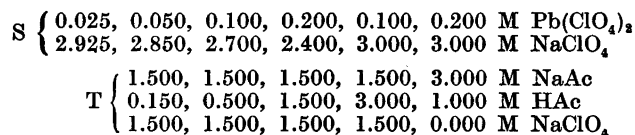


Fig. 4. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the lead acetate system. *a*: at different pH, $C_M = 0.100$. $C_A/C_{HA} = 10$ (\circ); $C_A/C_{HA} = 3$ (\square); $C_A/C_{HA} = 1$ (\triangle); $C_A/C_{HA} = 1/2$ (∇). *b*: at different central ion concentrations, $C_A = 1.500$, $C_{HA} = 0.500$. $C_M = 0.025$ (\triangle); $C_M = 0.050$ (\circ); $C_M = 0.100$ (\square); $C_M = 0.200$ (∇). Additions with the sodium ion concentration constant and $C_M = 0.100$ (\blacksquare).

Table 6. The reaction heats, corrected for dilution, obtained at the titrations of the solutions. C_A and C_{HA} are the acetate ion in the T

		$\Sigma Q_{\text{corr.}}$								
C_M (M)		0.025	0.050	0.100	0.200	0.500				
C_A (M)		1.500	1.500	1.500	1.500	1.500				
C_{HA} (M)		0.500	0.500	0.500	0.500	0.500				
C_A/C_{HA}		3	3	3	3	3				
v (ml)										
1.005			0.069	0.105	0.103					
2.009	0.130	0.125	0.193	0.195	0.311	0.294	0.449	0.444	0.368	0.378
4.018	0.218	0.222	0.357	0.352	0.596	0.572	0.900	0.876	0.660	0.686
6.027	0.290	0.297	0.500	0.482	0.858	0.845	1.320	1.312	0.917	0.928
8.036	0.354	0.365	0.624	0.604	1.117	1.090	1.751	1.739	1.129	1.135
10.045	0.414	0.423	0.744	0.717	1.365	1.335	2.133	2.097	1.310	1.318
12.054	0.459	0.472	0.845	0.804	1.600	1.560	2.519	2.489	1.514	1.536
14.063			0.930	0.896	1.820	1.789	2.894	2.879	1.713	1.747
16.072			1.014	0.967	2.025	2.013	3.259	3.280	1.881	1.925
18.081			1.108	1.049	2.227	2.218	3.632	3.672	2.048	2.109
20.090					2.419	2.418	4.042	4.075	2.184	2.271
22.099							4.409	4.462		

* The sodium ion concentration is constant, 3.000 M.

The experimental values are given in Tables 1 and 6, and the Δh_v -functions are plotted *versus* \bar{n} in Figs. 4 a and 4 b. No effect from hydrolysis of this system was found when the pH varied (see Fig. 4 a), and furthermore the extremely good agreement between measurements with buffers of different pH but the same C_A would indicate that the correction technique for dilution heats could be used at least for $C_M \leq 0.050$ M. Measurements with different C_M gave a distinct but small dependence in the Δh_v -values (see Fig. 4 b). However, titrations with constant sodium ion concentration, $[Na^+] = 3.000$ M, gave a reversed variation (see Fig. 4 b). No polynuclear species were reported from the potentiometric investigation of this system,¹⁰ and the dependence of C_M is here, as for previous systems, most likely caused by effects from variations of ionic strength at the complex formation. The values of ΔG_i° , ΔH_i° , and ΔS_i° are collected in Table 8 with their estimated errors.

Accuracy of the results. For these systems the error in $Q_{\text{corr.}}$ is difficult to estimate. Besides the random errors in Q_x and $Q_{\text{dil.}}$ — the reproducibility is better than ± 0.02 cal — there may be systematic errors in $Q_{\text{dil.}}$, as described before. But this influences mostly the values of the third and fourth complexes, which are formed only to a small extent, and furthermore the errors diminish when C_M decreases.

The error in the enthalpy changes depends also on the accuracy of the stability constants. For all these acetate systems only the first two constants

lead(II) system at various C_M and pH. C_M is the initial lead ion concentration in the S and acetic acid concentrations, respectively, solutions.

(cal)										
0.100		0.050		0.100		0.100		0.100	0.100 ^a	0.200 ^a
3.000		1.500		1.500		1.500		1.500	1.500	1.500
1.000		1.500		0.150		1.500		3.000	0.500	0.500
3		1		10		1		1/2	3	3
0.605	0.589	0.212	0.120	0.243	0.251	0.350	0.350	0.326	0.108	0.098
1.142	1.147	0.385	0.387	0.500	0.497	0.649	0.668	0.580	0.201	0.183
1.659	1.659	0.524	0.524	0.755	0.752	0.916	0.950	0.822	0.246	0.267
2.140	2.120	0.659	0.652	1.005	1.006	1.161	1.217	1.029	0.242	0.303
2.553	2.563	0.776	0.760	1.245	1.246	1.401	1.457	1.204	0.199	0.312
2.964	3.001	0.879	0.856	1.469	1.505	1.625	1.706	1.383	0.146	0.284
3.343	3.389	0.972		1.678	1.731	1.850	1.924	1.552	0.084	0.243
3.734	3.780			1.873	1.942	2.048	2.141	1.704	-0.002	0.186
4.115	4.164			2.054	2.145	2.225	2.345	1.836		0.090
4.491	4.528			2.212	2.332	2.407	2.528	1.974		-0.009
4.846	4.873									

could be determined with high accuracy. Then effects from variations of liquid junction potentials, complex formation between $\text{Ac}^- - \text{HAc}$, and changing activity factors would influence the stability constants.^{8,19} In fact, the formation of the fourth complex species is not even certainly proved either with potentiometric measurements or with this calorimetric investigation for any of these systems. However, no systematic errors are found in the differences $Q_{\text{corr.}} - Q_{\text{corr., calc.}}$ (see Table 7). The enthalpy and entropy changes for the first two steps can thus be determined with a satisfactory accuracy and a reasonable estimation can be made even for the third step.

DISCUSSION

The free energy, enthalpy, and entropy changes found for the stepwise formation of the investigated complex systems are collected in Table 8. As explained earlier the errors in the third step are greater than usual and for the fourth one, no reliable values at all can be given for the enthalpy and entropy changes. For the first two steps, however, the thermodynamic values can be determined with good accuracy, and they lead to the following conclusions.

a. The results in this investigation are not opposed to previous results. Values calculated from the data of Tanaka *et al.*^{3,4} are too uncertain, even to

Table 7. The differences ($Q_{\text{corr.}} - Q_{\text{corr., calc.}}$) for the four acetate systems. For every system two representative series are given.

		$Q_{\text{corr.}} - Q_{\text{corr., calc.}}$ (cal)							
Metal ion		Cu^{2+}		Zn^{2+}		Cd^{2+}		Pb^{2+}	
C_M (M)		0.050	0.100	0.050	0.050	0.030	0.090	0.050	0.100
v (ml)									
2.009		0.000	-0.005	-0.006	0.004	-0.016	0.058	-0.001	0.018
4.018		-0.005	0.007	-0.004	-0.004	-0.008	-0.027	0.004	-0.017
6.027		0.014	0.004	-0.008	-0.008	0.020	0.007	-0.003	0.012
8.036		-0.006	-0.001	0.003	0.003	0.009	0.029	-0.005	0.011
10.045		-0.011	-0.013	-0.020	-0.000	0.020	0.003	-0.022	-0.031
12.054		0.005	0.010	-0.006	0.004	0.005	0.037	0.025	-0.011
14.063		0.005	-0.007	-0.003	0.007	0.009	0.042	0.021	-0.025
16.072		-0.001	0.008	-0.011	-0.001	-0.010	0.062	-0.005	0.000
18.081		0.002	-0.003	0.001	0.001		0.024	-0.000	0.004
20.090		-0.003	-0.000	-0.006	-0.006		-0.009	-0.015	0.017

Table 8. The stability constants used and the computed values of free energy, enthalpy, and entropy changes for the stepwise reactions of the four acetate systems are tabulated. All values are given with their estimated errors.

Metal ion		Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
β_j (M^{-1})	$j = 1$	75 ± 0.5	8.8 ± 0.3	20 ± 1	214 ± 1
	2	1310 ± 12	22 ± 2	190 ± 20	3990 ± 25
	3	3830 ± 100	71 ± 10	260 ± 50	3850 ± 110
	4	2120 ± 190	—	100 ± 50	736 ± 120
$-\Delta G_j^\circ \times 10^{-3}$ (cal mole $^{-1}$)	1	2.56 ± 0.01	1.29 ± 0.02	1.78 ± 0.03	3.18 ± 0.01
	2	1.69 ± 0.01	0.54 ± 0.05	1.33 ± 0.07	1.73 ± 0.01
	3	0.64 ± 0.02	0.69 ± 0.11	0.19 ± 0.14	-0.02 ± 0.02
	4	-0.35 ± 0.06	—	-0.57 ± 0.43	-0.98 ± 0.11
$-\Delta H_j^\circ \times 10^{-3}$ (cal mole $^{-1}$)	1	-1.04 ± 0.02	-2.04 ± 0.03	-1.46 ± 0.02	0.06 ± 0.01
	2	-0.41 ± 0.04	-3.22 ± 0.15	-0.84 ± 0.09	0.09 ± 0.03
	3	-0.07 ± 0.11	-1.15 ± 0.19	-0.41 ± 0.19	0.96 ± 0.21
	4	—	—	—	—
ΔS_j° (cal mole $^{-1}$ degree $^{-1}$)	1	12.1 ± 0.1	11.2 ± 0.2	10.9 ± 0.2	10.5 ± 0.1
	2	7.1 ± 0.2	12.5 ± 0.5	7.3 ± 0.5	5.5 ± 0.2
	3	2.4 ± 0.5	6.1 ± 0.8	2.0 ± 1.1	-3.3 ± 0.8
	4	—	—	—	—

the sign, for a comparison, but for the copper(II) system the value of $-\Delta H_1^\circ$ is in good agreement with that of -1.01×10^3 (cal mole $^{-1}$) found by Pockock and Rossotti⁵ and the resemblance with the lanthanoide acetate complexes⁶ is very striking.

b. Like the lanthanoide acetates investigated by Grenthe,⁶ but in contrast to most of the cadmium(II) halide¹ and pseudo halide systems,² the complex formation here, where oxygen is the ligand atom, is stabilized predominantly by the entropy term. The reactions are nearly all endothermic. The entropy term, however, is not so great as for the lanthanoide systems, probably depending on the difference in charge of the metal ions.

c. The variation in stability between the four acetate systems investigated chiefly depends on the enthalpy term, just as for the halide¹ and pseudo halide systems.²

d. The thermodynamic properties investigated could not in a simple way be related to either atomic number and ionic radius or ionisation potentials and electronegativity of the metal ions for these four acetate systems. The $-ΔG_j^\circ$ and $-ΔH_j^\circ$ -values increase mainly in the order zinc, cadmium, copper, and lead and the $ΔS_j^\circ$ -values are almost constant for each step, respectively, with some exceptions. The position of the copper system may depend on its square planar configuration or ligand field stabilisation energy.

e. For each of the acetate systems except the zinc one, the $-ΔG_j^\circ$ and $ΔS_j^\circ$ values decrease progressively as j increases, whilst the $-ΔH_j^\circ$ values increase. The extreme values of $-ΔH_2^\circ$ and $ΔS_2^\circ$ for the zinc(II) system are interesting, and could be an indication of the greater tendency for the zinc(II) ion to give tetrahedral complexes.²⁰

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