# Thermochemical Studies of Hydrolytic Reactions

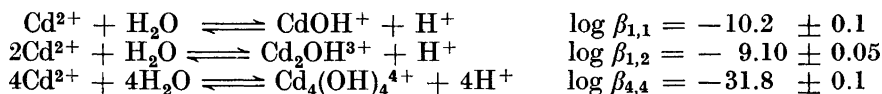## 4. A Thermochemical Study of Hydrolysed Cd(ClO₄)₂ Solutions

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The enthalpy and entropy changes of the hydrolysis reactions of $Cd^{2+}$ in 3 M $(Li)ClO_4$ at 25°C have been determined by enthalpy titrations of hydrolysed $Cd(ClO_4)_2$ solutions. Using the hydrolysis mechanism proposed by Biedermann and Ciavatta [1] in interpreting the heat data, the following results were obtained:

| | $\Delta H$, kcal | $\Delta S$, e.u. |
|---|---|---|
| $Cd^{2+} + H_2O \rightleftharpoons CdOH^+ + H^+$ | 13.1 ± 2.1 | −2.7 ± 6.9 |
| $2\,Cd^{2+} + H_2O \rightleftharpoons Cd_2OH^{3+} + H^+$ | 10.9 ± 0.2 | −5.1 ± 0.8 |
| $4\,Cd^{2+} + 4H_2O \rightleftharpoons Cd_4(OH)_4^{4+} + 4H^+$ | 40.6 ± 1.1 | −9.4 ± 3.7 |

The hydrolysis reactions of the $Cd^{2+}$ ion (25°C, 3 M $(Li)ClO_4$) have been studied with emf methods by Biedermann and Ciavatta.[1] They explained their emf data by assuming the equilibria

$$
\begin{aligned}
Cd^{2+} + H_2O &\rightleftharpoons CdOH^+ + H^+ & \log \beta_{1,1} &= -10.2 \pm 0.1 \\
2Cd^{2+} + H_2O &\rightleftharpoons Cd_2OH^{3+} + H^+ & \log \beta_{1,2} &= -9.10 \pm 0.05 \\
4Cd^{2+} + 4H_2O &\rightleftharpoons Cd_4(OH)_4^{4+} + 4H^+ & \log \beta_{4,4} &= -31.8 \pm 0.1
\end{aligned}
$$

No thermochemical data are available for these reactions and the present investigation was made in order to obtain such information.
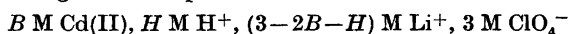
## EXPERIMENTAL

The heat measurements were performed as enthalpy titrations, using a calorimeter described earlier.[2] The calorimeter vessel was charged with a hydrolysed $Cd(ClO_4)_2$ solution, S, volume $V_0 = 224.53$ ml, and titrated with an acid solution, T, from the thermostated buret.

The hydrolysed cadmium perchlorate solutions were prepared by dissolving a small excess of CdO (Matheson Coleman & Bell) in $HClO_4$. The solution was left overnight with continuous stirring and with purified nitrogen gas bubbling through it to expel $CO_2$. After addition of lithium perchlorate and dilution to the desired volume, the small excess

of $Cd(OH)_2$ was removed by filtration. These manipulations were carried out under an atmosphere of purified nitrogen. The cadmium concentration of the solution was determined gravimetrically by precipitating $CdNH_4PO_4H_2O$, according to Winkler.[3] The analytical excess of hydrogen ions, $H = [ClO_4^-] - 2[Cd(II)] - [Li^+]$, was obtained directly from the enthalpy titrations, as will be shown later.

The acid solutions, T, were prepared by dissolving a weighed amount of CdO in a known amount of standard perchloric acid.

The general composition of the solutions S and T were

$B$ M Cd(II), $H$ M $H^+$, $(3 - 2B - H)$ M $Li^+$, 3 M $ClO_4^-$

The values of $B$, the total Cd(II) concentration, and $H$, the analytical excess of hydrogen ions, used in the different experiments are given in Table 1, where $H_T = H$ of the buret solution; $H_S =$ initial value of $H$ in the calorimeter solution; $B_T = B$ of the buret solution; $B_S =$ initial value of $B$ in the calorimeter solution.

*Table 1.* Survey of titrations.

*Experiment No.*

|  | 1a,b | 2 | 3a,b | 4a,b |
|---|---|---|---|---|
| $B_S$, M | 1.015 | 0.5846 | 0.5852 | 0.2892 |
| $B_T$, M | 1.000 | 0.5800 | 0.5800 | 0.2886 |
| $H_S$, M | −0.0159 | −0.00720 | −0.00848 | −0.00317 |
| $H_T$, M | 0.3008 | 0.0800 | 0.1000 | 0.0500 |

Fig. 1 shows $\sum Q$, the cumulative heat effect during a typical experiment, as a function of $v$, the volume of solution added from the buret. The intersection of the two lines in Fig. 1 gives the point where all the hydrolysed Cd(II) has been converted to $Cd^{2+}$ aq. From the value of $v$ at the intersection point, $v_e$, we can directly calculate the analytical hydrogen ion excess in the initial solution, $H_S$, from

$$-H_S = v_e H_T / V_0$$

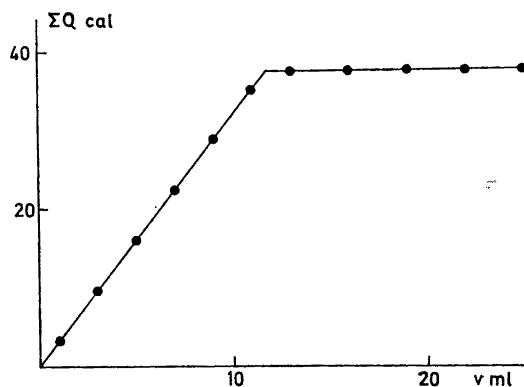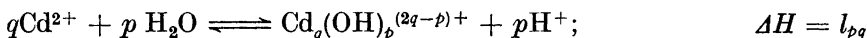where $H_T$ is known from the preparation of the solution T.



*Fig. 1.* $\sum Q$, the cumulative heat effect as a function of the added volume, $v$, during a typical experiment.

## RESULTS AND CALCULATIONS

The reactions we have been studying are

$$q\text{Cd}^{2+} + p\,\text{H}_2\text{O} \rightleftharpoons \text{Cd}_q(\text{OH})_p{}^{(2q-p)+} + p\text{H}^+; \qquad\qquad \Delta H = l_{pq}$$

$\Delta H$ for this reaction may be called the relative molar enthalpy $l_{pq}$ of the complex $\text{Cd}_q(\text{OH})_p{}^{(2q-p)+}$ and its equilibrium constant will be called $\beta_{pq}$. The values for the $\beta_{pq}$ were taken from the emf work of Biedermann and Ciavatta.[1]

After an addition of $v$ ml of the acid solution T to the initial volume $V_0$ ml (always 224.53 ml) of the hydrolysed solution S the total excess enthalpy, $L$, in the calorimeter may be defined as

$$L = V\sum c_{pq}l_{pq}$$

where $V = V_0 + v$ and $c_{pq}$ is the concentration of $\text{Cd}_q(\text{OH})_p{}^{2q-p)+}$. If $L'$ and $V'$ are the excess enthalpy and volume before an addition and $L''$ and $V''$ the excess enthalpy and volume after the addition from the buret, the heat evolved, $Q$, is

$$Q = L' - L'' + (V'' - V')l_T$$

where $l_T$ (cal/l) is the excess enthalpy of solution T ("heat of dilution"). The heats of dilution were found from experiments to be quite negligible.

Pairs of $(Q,v)$-values are obtained as a result of an enthalpy titration. To find the "best" values for the unknown $l_{pq}$ we have used the calorimeter version of the least squares computer program LETAGROPVRID [4,5] using a CDC 3600 computer. With the program LETAGROPVRID the computer searches for the set of values of the unknown parameters, $k_i$, which will minimize the error square sum

$$U = \sum(Q_{\text{calc}} - Q)^2$$

The input information to the computer is the values of the equilibrium constants $\beta_{pq}$ and estimates of the enthalpies $l_{pq}$ (common for all data), $B_S$, $B_T$, $H_S$, $H_T$, $V_0$ (for each titration) and $v$ and $Q$ (for each point in the titration). The output information is a set of $l_{pq}$ with their standard deviations and the standard deviation in the $Q$ measurements, $\sigma(Q)$.

In order to check the graphical determination of $H_S$, we assumed a small error in $H_S$, $\delta H_S$, in each titration. These errors, $\delta H_S$, were also treated as unknown constants to be determined.

From the LETAGROPVRID treatment of the heat data we obtained the following result,

$$
\begin{aligned}
l_{11} &= 13.1 \;\pm\; 0.7 \;\;\text{kcal/mole} \\
l_{12} &= 10.91 \pm 0.07\;\text{kcal/mole} \qquad\qquad \sigma(Q) = 0.04\;\text{cal} \\
l_{44} &= 40.56 \pm 0.35\;\text{kcal/mole}
\end{aligned}
$$

The deviations given are $\sigma$, the standard deviation calculated by LETA-GROPVRID.

The standard deviations for $l_{11}$ and $l_{44}$ are much larger than that for $l_{12}$ and that is expected as the principal product of hydrolysis is the species $\text{Cd}_2\text{OH}^{3+}$.

The difference between the measured $Q$-values and the $Q$-values calculated with the $l_{pq}$ above are shown in Table 2. No significant deviations seem to be present. The corrections $\delta H_S$, estimated by the computer are also given in Table 2. They are apparently small.

It was necessary to perform experiments at different metal concentrations to be able to determine all the $l_{pq}$. As cadmium(II) is hydrolysed to a very small extent the free metal concentration, $b$, is very close to the total metal concentration $B$. From this it follows that the ratio

$$\frac{c_{12}}{c_{11}} = \frac{\beta_{12}}{\beta_{11}} \cdot b \approx \frac{\beta_{12}}{\beta_{11}} \cdot B$$

is constant at constant $B$. Thus it is not possible to determine $l_{11}$ and $l_{12}$ from one titration with a constant $B$ value.

*Table 2.* Survey of measurements. Values of $v$ [ml], $Q$ [cal], $(Q_{calc} - Q)$ [cal].

*Titr 1a.* $B_S = 1015$ mM, $H_S = -15.90$ mM, $\delta H_S = (0.07 \pm 0.01)$ mM

$v, Q, (Q_{calc} - Q)$; 1.00, 3.15, 0.04; 3.00, 6.43, 0.00; 5.00, 6.54, $-0.04$; 7.00, 6.58, $-0.01$; 9.00, 6.70, $-0.07$; 11.00, 6.62, 0.04; 13.00, 2.71, 0.00; 16.00, 0.00, 0.00; 19.00, 0.00, 0.00; 22.00, 0.00, 0.00; 25.00, 0.00, 0.00;

*Titr 1b.* $B_S = 1015$ mM, $H_S = -15.90$ mM, $\delta H_S = (0.08 \pm 0.02)$ mM

$v, Q, (Q_{calc} - Q)$; 2.00, 6.38, 0.02; 4.00, 6.49, $-0.03$; 6.00, 6.46, 0.08; 8.00, 6.65, $-0.04$; 10.00, 6.67, $-0.02$; 12.00 6.03, $-0.02$; 15.00, 0.03, $-0.02$; 18.00, 0.02, $-0.02$; 22.00, 0.02, $-0.02$;

*Titr 2.* $B_S = 584.6$ mM, $H_S = -7.20$ mM, $\delta H_S = (0.00 \pm 0.01)$ mM

$v, Q, (Q_{calc} - Q)$; 1.00, 0.85, 0.00; 3.00, 1.75, $-0.03$; 5.00, 1.71, 0.02; 7.00, 1.78, $-0.03$; 9.00 1.77, $-0.01$; 11.00, 1.78, $-0.02$; 13.00, 1.80, $-0.02$; 15.00, 1.81, $-0.02$; 17.00, 1.78, 0.00; 19.00, 1.74, 0.05; 21.00, 1.09, $-0.01$; 23.00, 0.05, $-0.05$; 25.00, 0.00, 0.00;

*Titr 3a.* $B_S = 585.2$ mM, $H_S = -8.48$ mM, $\delta H_S = (0.02 \pm 0.02)$ mM

$v, Q, (Q_{calc} - Q)$; 2.00, 2.11, 0.02; 4.00, 2.06, 0.08; 6.00, 2.16, 0.00; 8.00, 2.14, 0.04; 10.00, 2.17, 0.03; 12.00, 2.22, $-0.01$; 14.00, 2.22, 0.00; 16.00, 2.23, 0.01; 18.00, 2.12, 0.11; 20.00, 1.13, $-0.01$; 22.00, 0.00, 0.00;

*Titr 3b.* $B_S = 585.2$ mM, $H_S = -8.48$ mM, $\delta H_S = (-0.02 \pm 0.02)$ mM

$v, Q, (Q_{calc} - Q)$; 2.00, 2.18, $-0.05$; 4.00, 2.14, 0.00; 6.00, 2.15, 0.01; 8.00, 2.16, 0.02; 10.00, 2.21, $-0.01$; 12.00, 2.20, 0.01; 14.00, 2.21, 0.02; 16,00, 2.17, 0.06; 18.00, 2.14, 0.09; 20.00, 1.23, $-0.01$; 22.00, 0.01, $-0.01$;

*Titr 4a.* $B_S = 289.2$ mM, $H_S = -3.17$ mM, $\delta H_S = (-0.05 \pm 0.02)$ mM

$v, Q, (Q_{calc} - Q)$; 2.00, 1.16, $-0.07$; 4.00, 1.11, $-0.01$; 6.00, 1.11, 0.00; 8.00, 1.15, $-0.03$; 10.00, 1.19, $-0.06$; 12.00, 1.17, $-0.03$; 14.00, 1.04, 0.10; 16.00, 0.29, $-0.02$; 18.00, 0.00, 0.00; 20.00, 0.00, 0.00;

*Titr 4b.* $B_S = 289.2$ mM, $H_S = -3.17$ mM, $\delta H_S = (-0.03 \pm 0.02)$ mM

$v, Q, (Q_{calc} - Q)$; 2.00, 1.13, $-0.03$; 4.00, 1.16, $-0.06$; 6.00, 1.15, $-0.03$; 8.00, 1.18, $-0.06$; 10.00, 1.19, $-0.06$; 12.00, 1.19, $-0.05$; 14.00, 1.04, 0.10; 16.00, 0.21, $-0.01$; 18.00, 0.00, 0.00;
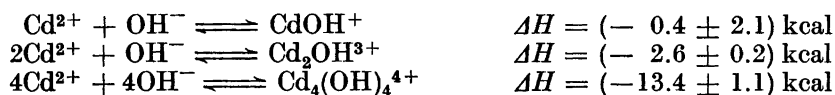
The thermochemical data for the hydrolytic reactions of Cd(II) have been summarised in Table 3. The deviations given are $3\sigma$.

*Table 3.*

| Reaction | $\Delta G$, kcal | $\Delta H$, kcal | $\Delta S$, e.u. |
|---|---|---|---|
| $Cd^{2+} + H_2O \rightleftharpoons CdOH^+ + H^+$ | $13.9 \pm 0.1$ | $13.1 \pm 2.1$ | $-2.7 \pm 6.9$ |
| $2Cd^{2+} + H_2O \rightleftharpoons Cd_2OH^{3+} + H^+$ | $12.41 \pm 0.07$ | $10.9 \pm 0.2$ | $-5.1 \pm 0.8$ |
| $4Cd^{2+} + 4H_2O \rightleftharpoons Cd_4(OH)_4^{4+} + 4H^+$ | $43.4 \pm 0.1$ | $40.6 \pm 1.1$ | $-9.4 \pm 3.7$ |

The heat of ionisation of water in 3 M $LiClO_4$ has been determined by means of enthalpy titrations of $\approx$ 5 mM LiOH (prepared by electrolysis) with 0.1 M $HClO_4$. The value obtained was $13.5 \pm 0.1$ kcal/mole, neglecting the probably very small dilution effects.

If the $\Delta H$-values for the reactions in Table 3 are combined with the $\Delta H$-value of $13.5 \pm 0.1$ kcal/mole for the ionisation of water in 3 M $LiClO_4$ we obtain:

$$Cd^{2+} + OH^- \rightleftharpoons CdOH^+ \qquad \Delta H = (-\ 0.4 \pm 2.1)\ kcal$$
$$2Cd^{2+} + OH^- \rightleftharpoons Cd_2OH^{3+} \qquad \Delta H = (-\ 2.6 \pm 0.2)\ kcal$$
$$4Cd^{2+} + 4OH^- \rightleftharpoons Cd_4(OH)_4^{4+} \qquad \Delta H = (-13.4 \pm 1.1)\ kcal$$

The thermochemical data for the reactions in which the polynuclear cadmium(II) species are formed from the monomer $CdOH^+$ are given in Table 4.

*Table 4.*

| Reaction | $\Delta G$, kcal | $\Delta H$, kcal | $\Delta S$, e.u. |
|---|---|---|---|
| $CdOH^+ + Cd^{2+} \rightleftharpoons Cd_2OH^{3+}$ | $-\ 1.5 \pm 0.2$ | $-\ 2.2 \pm 2.1$ | $-2.3 \pm\ 7.0$ |
| $4CdOH^+ \rightleftharpoons Cd_4(OH)_4^{4+}$ | $-12.2 \pm 0.3$ | $-11.8 \pm 4.3$ | $+1.3 \pm 14.4$ |

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