Studies on the Hydrolysis of Metal Ions
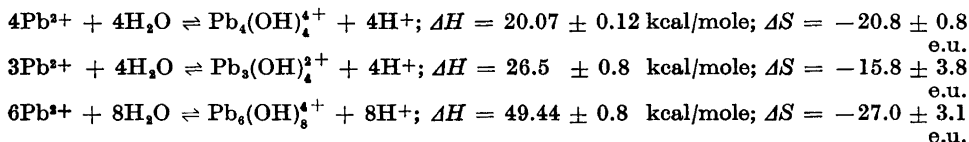
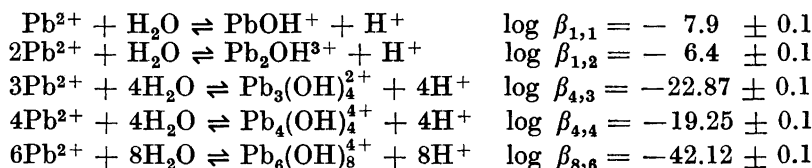## 42. A Thermochemical Study of Hydrolysed Pb(ClO$_4$)$_2$ Solutions

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The enthalpy and entropy changes of the main hydrolysis reactions of Pb^{2+} have been determined by enthalpy titrations with hydrolysed Pb(ClO$_4$)$_2$ solutions in 3 M (Na)ClO$_4$ at 25°C. The results obtained were:

$$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+; \quad \varDelta H = 20.07 \pm 0.12 \text{ kcal/mole}; \quad \varDelta S = -20.8 \pm 0.8 \text{ e.u.}$$

$$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+; \quad \varDelta H = 26.5 \pm 0.8 \text{ kcal/mole}; \quad \varDelta S = -15.8 \pm 3.8 \text{ e.u.}$$

$$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+; \quad \varDelta H = 49.44 \pm 0.8 \text{ kcal/mole}; \quad \varDelta S = -27.0 \pm 3.1 \text{ e.u.}$$

T he hydrolysis reactions of the Pb^{2+} ion have been studied with emf methods by one of the present authors [1,2]. The following species were identified and the numerical values of the corresponding formation constants in 3 M NaClO$_4$ medium were determined.

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^+ + H^+ \quad \log \beta_{1,1} = -7.9 \pm 0.1$$

$$2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+ \quad \log \beta_{1,2} = -6.4 \pm 0.1$$

$$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+ \quad \log \beta_{4,3} = -22.87 \pm 0.1$$

$$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+ \quad \log \beta_{4,4} = -19.25 \pm 0.1$$

$$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+ \quad \log \beta_{8,6} = -42.12 \pm 0.1$$

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

EXPERIMENTAL

The experiments were carried out in a calorimeter constructed by Dr. K. Schlyter. The calorimeter design and the experimental technique used with this calorimeter have been described in great detail by him[3]. In brief, a titration technique is used. The calorimeter vessel is charged with one of the reactants and the other reactant is added gradually from a thermostated buret. The change in temperature of the calorimeter contents is

determined after each addition from the buret and the temperature in the calorimeter is brought back to its initial value by a cooling device before a new addition is made.

The performance of the calorimeter was occasionally checked by test titrations with HCl. The heats of dilution of HCl found in these tests generally agreed to within 1 % with those calculated from the data given by Sturtevant [4]. This was considered sufficient for the present purpose.

The hydrolysed lead perchlorate solution was prepared by mixing calculated volumes of carefully analysed stock solutions of $Pb(ClO_4)_2$, NaOH and $NaClO_4$, in a volumetric flask in an atmosphere of nitrogen. Such solutions react with CO_2 and form lead hydroxide carbonates and must therefore be prepared and handled in an inert atmosphere. The hydrolysed solution was transferred with a calibrated pipet of ca 225 ml volume to the calorimeter vessel, which had been filled with N_2 beforehand. The stirrer in the vessel was provided with an air-tight seal, which prevented the contents of the calorimeter vessel from coming into contact with the CO_2 of the air.

The titrant was also mixed from stock solutions. The compositions of the solutions were chosen so that the total concentration $[Pb(II)] = B$, and $[ClO_4^-] = 3$ M were kept constant in each experiment. The addition of acid from the buret was continued till the heat evolved per addition was zero. This occurred when the hydrolysed lead species had been converted to Pb^{2+} and H_2O.

The values of B used were 0.08, 0.04, 0.02 and 0.01 M. For each value of B two titrations were made. Table 1 gives the analytical hydrogen ion excess of the starting solution in the calorimeter vessel, H_S, and of the titrating solution in the buret, H_T. The value of the analytical hydrogen ion excess, which usually is a negative number, in each point of a titration can be calculated from eqn. (1).

Table 1. Survey of titrations.

	$B = 0.08$ M	$B = 0.04$ M	$B = 0.02$ M	$B = 0.01$ M
H_S, M	-0.07096	-0.05297	-0.02592	-0.01299
H_T, M	0.8767	0.5971	0.3185	0.2844

Table 2. Data from titrations with $B = 0.02$ M.

v ml	Q cal	Q_{calc} cal	$Q - Q_{calc}$ cal
1	2.82	2.90	-0.08
3	5.60	5.54	0.06
5	4.85	4.89	-0.04
7	3.98	3.97	0.01
9	3.47	3.47	0.00
11	3.32	3.31	0.01
13	3.24	3.26	-0.02
15	3.26	3.23	0.03
17	3.30	3.22	0.08
2	5.72	5.72	0.00
4	5.32	5.27	0.05
6	4.35	4.43	-0.08
8	3.70	3.67	0.03
10	3.36	3.38	-0.02
12	3.30	3.27	0.03
14	3.26	3.24	0.02
16	3.26	3.22	0.04
18	3.29	3.22	0.07

$$H = (vH_T + V_oH_S)/(V_o + v) \tag{1}$$

V_o = initial volume of the solution in the calorimeter vessel (always 224.08 ml) and v = the volume of solution added from the buret.

The titrations with $B = 0.02$ M are given in Table 2 as an example of the experimental results obtained.

RESULTS AND CALCULATIONS

Two ml of acid were added each time from the buret. The heat evolved per addition, which was primarily registered as a deflection of a galvanometer light spot, was calculated as described by Schlyter [3].

If heats of dilution are neglected the heat evolved per addition, Q, is given by

$$Q = \sum_{p,q} \delta n_{pq}\, l_{pq} \tag{2}$$

δn_{pq} = the change of the number of moles of the species $Pb_q(OH)_p^{(2q-p)+}$ per addition of acid and l_{pq} = the enthalpy change (ΔH) of the reaction $q\ Pb^{2+} + p\ H_2O \rightleftarrows Pb_q(OH)_p^{(2q-p)+} + p\ H^+$. In eqn. (2) the Q are known from the calorimeter experiments. The δn_{pq} have been calculated from the known analytical compositions of the solutions and the equilibrium constants which were taken from the emf work [1,2]. We are thus presented with a set of linear equations in the unknowns, l_{pq}. The l_{pq} have been found by solving eqn. (2) by the method of least squares. The calculations were performed with an electronic computer (Ferranti-Mercury). The first step was the calculation of δn_{pq}. This was accomplished by a modified version of the program HALTA described by Ingri and Sillén [5]. The input information used with the program was B, H_T, H_S, v and V_o and the equilibrium constants. The computer then calculates the equilibrium concentrations of the various species for each point in a titration and the δn_{pq}. The δn_{pq} and the Q are then used with a "least squares program".

The first attempt to solve eqn. (2) for all the l_{pq} failed and indicated that with the present experimental accuracy l_{11} and l_{12} cannot be found. This situation is caused by the smallness of δn_{11} and δn_{12} which at most are 1 % of $\sum \delta n_{pq}$. The following approximation was therefore resorted to: l_{11} and l_{12} were set equal and were assumed to have the values 5 kcal/mole or 10 kcal/mole. Corrected values of Q were next calculated.

$$Q(\text{corrected}) = -Q - (\delta n_{11} + \delta n_{12})\ (5\ \text{or}\ 10) \tag{3}$$

The use of $\Delta H = 5$ and 10 kcal/mole was chosen from results with other systems studied by Schlyter. These studies have shown that the heat evolved per mole of OH^- lies in the range 5—10 kcal. This is also true for the present system as will be seen later. It should also be noted that these corrections are at most 2 % of Q.

With the corrected Q the following values of l_{pq} were found.
($l_{11} = l_{12} = 5$ kcal/mole)
$l_{44} = 20.07$ kcal/mole; $l_{43} = 26.53$ kcal/mole; $l_{86} = 49.44$ kcal/mole.
($l_{11} = l_{12} = 10$ kcal/mole)
$l_{44} = 20.13$ kcal/mole; $l_{43} = 26.03$ kcal/mole; $l_{86} = 49.85$ kcal/mole.
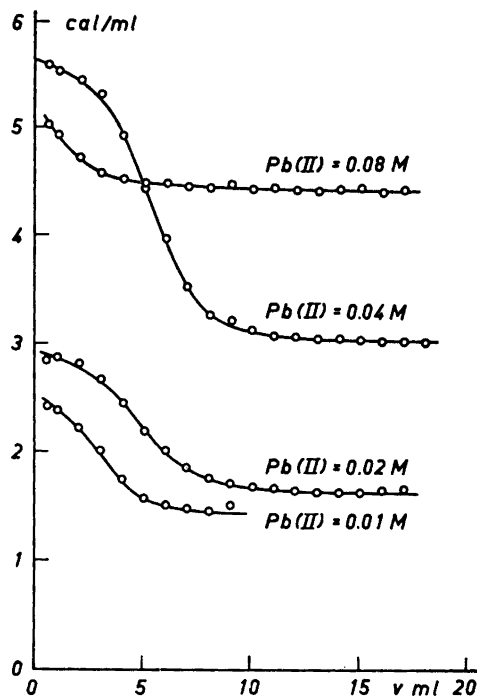
Fig. 1. Q and Q_{calc} (in cal per ml of acid added) as a function of v. The full lines represent Q_{calc} and the symbols represent Q.

$\Sigma(Q-Q_{calc})^2$ is smaller for the first set of l_{pq} and these will therefore be accepted as the best values. Justification for this choice also comes from the fact that the average value of the heat evolved per mole of OH^- is closer to 5 than to 10 kcal.

With the above values of l_{pq}, calculated values of the heat evolution per addition, Q_{calc}, have been obtained. These are given in the second column in Table 2. The difference between Q and Q_{calc} is given in the third column of the same table. The results are presented graphically in Fig. 1. From the figure it is seen that systematic deviations between Q and Q_{calc} are absent. The estimated standard deviation in Q, (Ref.[6]).

$$S = \pm \sqrt{\Sigma(Q-Q_{calc})^2/\nu} \qquad (4)$$

where ν is the number of degrees of freedom, is found to be $\pm$ 0.05 cal. This may be compared with a value of $\pm$ 0.04 cal calculated (at the 95 % confidence level) from the calorimetry measurement uncertainties (Ref.[3]).

The standard deviations in the l_{pq} given by the least squares treatment are smaller than the uncertainties arising from the choice of the value for l_{11} and l_{12}. We shall therefore assign an uncertainty in l_{pq} of twice the difference in l_{pq} between the two choices and obtain

$$l_{44} = 20.07 \pm 0.12 \ \text{kcal/mole}$$
$$l_{43} = 26.5 \ \pm 1 \quad \text{kcal/mole}$$
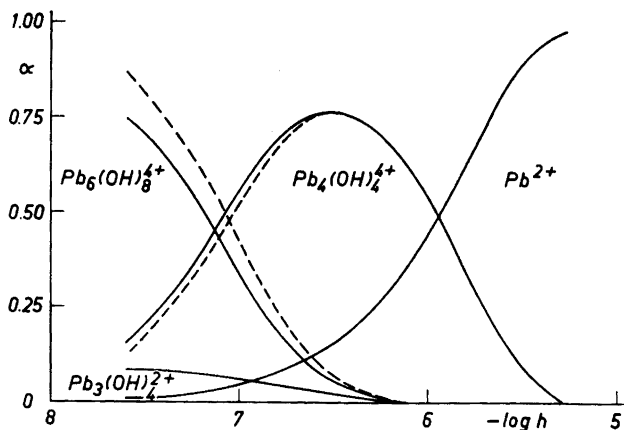$$l_{86} = 49.44 \pm 0.8 \ \text{kcal/mole}$$

Fig. 2. The relative amounts (α) of the hydrolysis products of Pb(II), at $B = 0.04$ M, expressed as percentages of the total lead. The amounts of $PbOH^+$ and Pb_2OH^{3+} are so small as not to appear in the figure. The full lines represent the distribution on the assumption that $Pb_3(OH)_4^{2+}$ is present, whereas the broken lines represent the distribution on the assumption that $Pb_3(OH)_4^{2+}$ is absent.

The interpretation of the emf measurements given in Ref. [1] leads to a distribution of the various lead species according to Fig. 2. $Pb_4(OH)_4^{4+}$ and $Pb_6(OH)_8^{4+}$ are the main hydrolysis products whereas the amount of $Pb_3(OH)_4^{2+}$ is relatively small. Since $[Pb_3(OH)_4^{2+}]$ is small, calculations, on the heat data have also been made on the assumption that this complex is not present. In order to find δn_{pq} the equilibrium constants found from the emf measure-
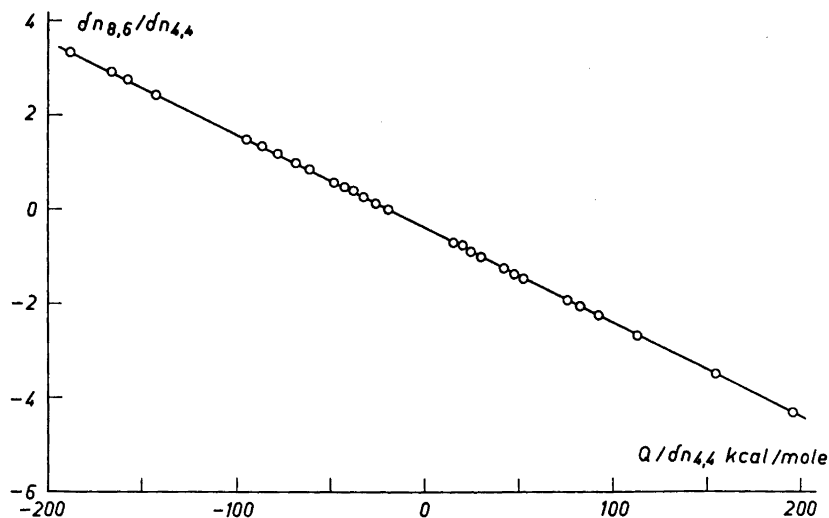

Fig. 3. Graphical determination of l_{44} and l_{86} according to eqn. (5a).

ments on this assumption were used, namely log $\beta_{4,4} = -19.25$ and log $\beta_{8,6} = -42.0$. In addition calculations were made where these constants were allowed to change by $\pm$ 0.2 log units. We have

$$Q = \delta n_{44}\, l_{44} + \delta n_{86}\, l_{86} \tag{5}$$

or

$$Q/\delta n_{44} = l_{44} + (\delta n_{86}/\delta n_{44})\, l_{86} \tag{5a}$$

The plots of eqn. (5a) were linear, Fig. 3, and for log $\beta_{4,4} = -19.25$ and log $\beta_{8,6} = -42.0$ the enthalpy changes were found to be

$$l_{44} = 20.08 \pm 0.15 \text{ kcal/mole}$$
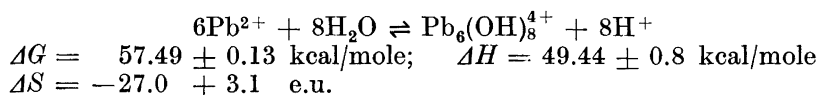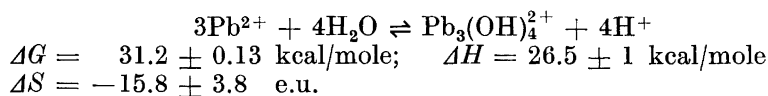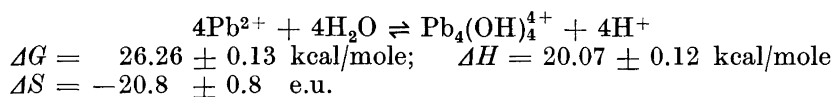$$l_{86} = 49.8 \pm 0.8 \text{ kcal/mole}$$

which are thus very close to the values found with the previous treatment. For the other pairs of log $\beta_{4,4}$ and log $\beta_{8,6}$ used the ΔH were the same within the limits of error given.

We find that enthalpy titrations of the present precision cannot be used to distinguish whether $Pb_3(OH)_4^{2+}$ is present or not. The reason for this is seen from the distribution curves in Fig. 2. The removal of $Pb_3(OH)_4^{2+}$ and the subsequent change of log $\beta_{8,6}$ has the effect that Pb(II) present as $Pb_3(OH)_4^{2+}$ will be reckoned as $Pb_6(OH)_8^{4+}$. The distribution curves for Pb^{2+} and $Pb_4(OH)_4^{4+}$ are changed but little. Very accurate heat data will be needed in order to distinguish whether $Pb_3(OH)_4^{2+}$ is negligible or whether $l_{86} \approx 2\, l_{43}$ unless external considerations indicate that $l_{86} \approx 2\, l_{43}$ is unreasonable.

The heat data cannot be used to confirm the presence of $Pb_4(OH)_4^{4+}$, although the horizontal parts of the curves in Fig. 1 strongly indicate the presence of only one complex. This situation arises from the fact that the heat data cannot be used to calculate (indirectly) the hydrogen ion concentration in the equilibrium solutions when the hydrolysis occurs in neutral or weakly acidic medium. For those metal ions which are strong acids, e.g. Bi^{3+}, and hydrolyse in strongly acidic solution the situation is different. In this case the heat data can be used to give information on the hydrolysis mechanism as will be shown in a later communication.

SUMMARY OF THE HEAT DATA

We have accepted the hydrolysis mechanism suggested by the emf measurements and find

$$4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$$
$\Delta G = 26.26 \pm 0.13$ kcal/mole; $\quad \Delta H = 20.07 \pm 0.12$ kcal/mole
$\Delta S = -20.8 \pm 0.8$ e.u.

$$3Pb^{2+} + 4H_2O \rightleftharpoons Pb_3(OH)_4^{2+} + 4H^+$$
$\Delta G = 31.2 \pm 0.13$ kcal/mole; $\quad \Delta H = 26.5 \pm 1$ kcal/mole
$\Delta S = -15.8 \pm 3.8$ e.u.

$$6Pb^{2+} + 8H_2O \rightleftharpoons Pb_6(OH)_8^{4+} + 8H^+$$
$\Delta G = 57.49 \pm 0.13$ kcal/mole; $\quad \Delta H = 49.44 \pm 0.8$ kcal/mole
$\Delta S = -27.0 \pm 3.1$ e.u.

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