Thermochemical Studies of Hydrolytic Reactions

## 5. A Thermochemical Study of Hydrolysed Cu(ClO$_4$)$_2$ Solutions

ROBERT ARNEK and C. C. PATEL*

Department of Inorganic Chemistry, The Royal Institute of Technology (KTH), Stockholm 70, Sweden

Enthalpy titrations have been performed with hydrolysed Cu(ClO$_4$)$_2$ solutions (25°C, 3 M (Na)ClO$_4$). Assuming the hydrolysis reaction and equilibrium constant proposed by Clara Berecki-Biedermann[1] we obtained the following result:

$$2Cu^{2+} + 2H_2O \rightleftharpoons Cu_2(OH)_2^{2+} + 2H^+ \quad \Delta H° = 15.8 \text{ kcal/mole}$$
$$\Delta S° = 4.4 \text{ e.u.}$$
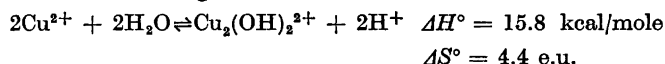
The hydrolysis equilibria of the Cu(II) ion in 3 M (Na)ClO$_4$ medium at 25°C were studied in 1955 by C. Berecki-Biedermann[1] with emf methods. The range of total Cu concentrations studied was 10—100 mM. The results were explained assuming the equilibrium

$$2Cu^{2+} + 2H_2O \rightleftharpoons Cu_2(OH)_2^{2+} + 2H^+ \qquad \log K = -10.6 \pm 0.1$$
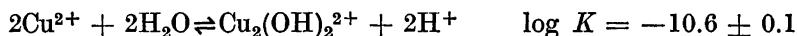
From Pedersen's[2] measurements on Cu(NO$_3$)$_2$ solutions the equilibrium constant for the mononuclear step $Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+$ was estimated by Berecki-Biedermann to be (1.0 ± 0.2) × 10^{-8} M.

No thermochemical data are available for hydrolysed copper salt solutions. The present investigation was undertaken in order to obtain such data.

EXPERIMENTAL

The calorimetric technique used in this work is the one earlier described by Arnek and Kakolowicz.[3]

Copper(II) perchlorate was prepared by dissolving CuO in excess of HClO$_4$ and recrystallizing once. A stock solution of Cu(ClO$_4$)$_2$ was then prepared and made slightly acidic (pH ≈ 3) by adding dilute perchloric acid. The copper(II) content of the stock solution was determined by electrodeposition.

---

* Present address: Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India.
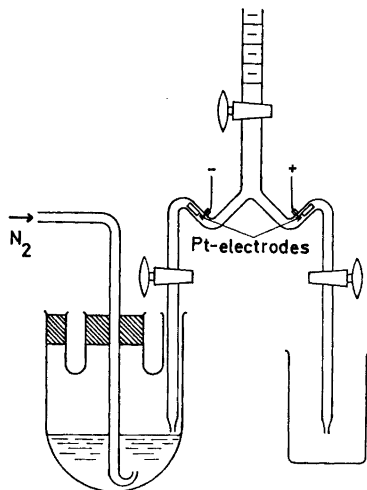
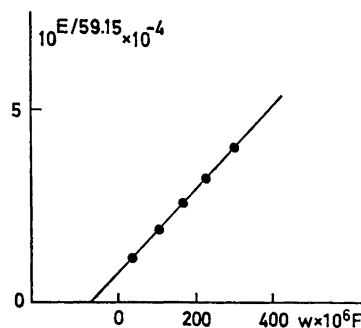Fig. 1. Arrangement for the preparation of hydrolysed solutions.

Fig. 2. Gran diagram for the determination of H_0'.

Cu(II) ion behaves as a weak acid and its hydrolysis takes place at log $h < -4$. In the preparation of hydrolysed Cu(II) solutions it is therefore most important to avoid the introduction of protolysing impurities, such as CO_2. For the preparation of the hydrolysed Cu(II) solutions, we used a method developed by Biedermann and Othaki,[4] which they will describe in detail in a forthcoming publication. An initially unhydrolysed solution of the general composition: B M Cu(II), H M H^+, $(3-2B-H)$ M Na^+, 3 M ClO_4^- was prepared. The acidity of this solution was decreased by adding to it a weak solution of NaOH (in 3 M $NaClO_4$), prepared in a specially designed apparatus (shown schematically in Fig. 1). The apparatus consists of a buret, equipped with two tips in each of which is sealed a platinum electrode. The electrodes are connected to the + and − pole of a constant current coulometer. The buret is filled with a 3 M $NaClO_4$ solution, which is allowed to run slowly with about the same speed from the two tips of the buret. Then the electrolysis is started with a current of about 60 mA. At the − pole (the left tip in Fig. 1) the reaction $H_2O + e^- \rightarrow OH^- + \frac{1}{2}H_2(g)$ takes place. The weak alkaline solution thus formed drops continuously into the initially unhydrolysed $Cu(ClO_4)_2$ solution, until a precipitate is formed. Purified nitrogen gas is bubbled through the solution all the time. The saturated hydrolysed solution is left overnight with continuous nitrogen stirring and is then filtered the next day through a glass filter. The solution is then transferred to the calorimeter vessel, which had been filled with N_2 beforehand, and the enthalpy titration performed.

The heat experiments consist of titrations in which successive additions of v ml of an acid solution T are made, from a thermostated buret, to V_0 ml ($V_0 = 224.53$ ml) of the hydrolysed solution S contained in the calorimeter. The titration is continued until the hydrolysed Cu(II) is converted to Cu^{2+}(aq). If the initial hydrogen excess of the hydrolysed solution is denoted by H_0, H at each point can be calculated from

$$H = \frac{V_0H_0 + vH_T}{V_0 + v}$$

H_0 was determined indirectly by determining H of the final calorimeter solution, H_0', by coulometric titration. H was increased stepwise by constant current coulometric oxidation and the hydrogen ion concentration, $h = H$, was measured by means of a glass electrode. The coulometric circuit consisted of

$-Pt\,|\,test\ solution\,|\,3.000\ M\ NaClO_4\,|\,2.900\ M\ NaClO_4,\ 0.100\ M\ AgClO_4\,|\,Ag+$

The hydrogen ion concentration, h, was measured by means of the cell

$$-SE\,|\,test\ solution\,|\,GE\ +$$

where GE denotes a glass electrode and SE the reference half cell AgCl,Ag | 2.990 M $NaClO_4$, 0.01 M NaCl | 3.000 M $NaClO_4$ |.

During the coulometric titrations the following equations are valid

$$H = H_0' + \frac{w}{V_0 + v}$$

$$E = E_0 + 59.15\ \log\ h$$

where H_0' is the value of H in the final calorimeter solution and w the number of Faradays passed through the solution. H_0' was calculated by means of a Gran plot, $10^{E/59.15}$ vs. w (Fig. 2): the intersection of the straight line with the w-axis gives the quantity $H_0(V_0 + v)$. The initial hydrogen excess, H_0, of the hydrolysed solution was then calculated from

$$H_0 = \frac{H_0'(V_0 + v) - vH_T}{V_0}$$

The values for B, the total Cu(II) concentration, and H, the analytical hydrogen excess, for the different titrations are given in Table 1.

Table 1. Survey of titrations.

	Titration No.		
	1	2	3
B_S, M	0.1586	0.1045	0.0738
B_T, M	0.000	0.000	0.000
H_S, M	-0.00238	-0.00198	-0.00114
H_T, M	0.05752	0.05752	0.05752

RESULTS AND CALCULATIONS

The reactions we have studied can be written

$$q\mathrm{Cu}^{2+} + p\mathrm{H_2O} \rightleftharpoons \mathrm{Cu}_q(\mathrm{OH})_p{}^{(2q-p)+} + p\mathrm{H}^+;\ \varDelta H = l_{pq}$$
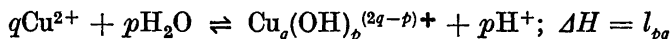
$\varDelta H$ for this reaction may be called the relative molar enthalpy l_{pq} of the complex $\mathrm{Cu}_q(\mathrm{OH})_p{}^{(2q-p)+}$ and its equilibrium constant will be called β_{pq}. The value for β_{pq} was taken from the emf work of Berecki-Biedermann.[1]

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

$$L = V \Sigma c_{pq} \cdot l_{pq}$$

where c_{pq} is the concentration of $\mathrm{Cu}_q(\mathrm{OH})_p{}^{(2q-p)+}$ and $V = V_0 + v$.

If L' and V' are the excess enthalpy and volume before, and L'' and V'' the excess enthalpy and volume after, an addition from the buret, the heat evolved is

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

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

Pairs of (Q,v) values are obtained as 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 [5,6] 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

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

The input information used with the program in our case is the equilibrium constants β_{pq} and estimates of the enthalpies l_{pq} (common for all data), B_S, B_T, H_S, H_T, and V_0 (for each titration), 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 (σ_Q).

In order to check the analytical H_0 values, we assumed that there is a small analytical error, δH_S, in H_0 for each titration. These systematic errors, δH_S, were also treated as unknown constants to be determined.

From the LETAGROPVRID treatment of the heat data we obtained the value 15.8 ± 0.2 kcal/mole for l_{22}. It proved impossible to determine l_{11} from our data. The species CuOH$^+$ is present in too low concentration to give an appreciable contribution to the measured heat effect. The standard deviation in the Q measurements was $\sigma_Q = 0.03$ cal.

Table 2. Survey of measurements.

Values of v [ml], Q [cal], $(Q_{calc}-Q)$ [cal]

Titr. 1. $B_S = 158.6$ mM, $H_S = -2.38$ mM, $\delta H_S = (0.036 \pm 0.034)$ mM, v, Q, $(Q_{calc}-Q)$; 2.00, 0.92, -0.02; 4.00, 0.92, -0.02; 6.00, 0.93, -0.04; 8.00, 0.88, -0.01; 10.00, 0.57, 0.02; 12.00, 0.11, -0.07; 14.00, 0.00, 0.00;

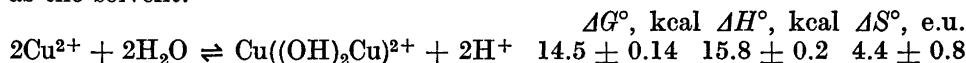*Titr. 2.* $B_S = 104.5$ mM, $H_S = -1.98$ mM, $\delta H_S = (0.00 \pm 0.046)$ mM, v, Q, $(Q_{calc}-Q)$; 2.00, 0.89, 0.01; 4.00, 0.87, 0.03; 6.00, 0.92, -0.03; 8.00, 0.71, 0.05; 10.00, 0.13, -0.05; 12.00, 0.05, -0.05;

Titr. 3. $B_S = 73.8$ mM, $H_S = -1.14$ mM, $\delta H_S = (0.014 \pm 0.016)$ mM, v, Q, $(Q_{calc}-Q)$; 2.00, 0.88, 0.02; 4.00, 0.84, 0.02; 6.00, 0.26, 0.00; 8.00, 0.04, -0.03; 10.00, 0.02, -0.02;

In Table 2 are given the experimental data, v [ml], Q [cal], together with the deviation between the calculated and measured heat, $(Q_{calc}-Q)$ [cal]. For each titration the small correction, δH_S, to the analytical hydrogen excess H_0, estimated by the computer, is also given. The agreement between the calculated and experimental data seems to be satisfactory, even for titration No. 1 where the B value 0.1586 M lies outside the concentration range studied by Berecki-Biedermann.

The thermochemical data for the hydrolysis of Cu(II) are given below. The zero superscript used with ΔG, ΔH, and ΔS means that the standard

states are hypothetical ideal one molar solutions of the solutes in 3 M (Na)ClO$_4$ as the solvent.

$$\Delta G°, \text{ kcal} \quad \Delta H°, \text{ kcal} \quad \Delta S°, \text{ e.u.}$$
$$2Cu^{2+} + 2H_2O \rightleftharpoons Cu((OH)_2Cu)^{2+} + 2H^+ \quad 14.5 \pm 0.14 \quad 15.8 \pm 0.2 \quad 4.4 \pm 0.8$$

The heat of ionisation of water in 3 M NaClO$_4$ has been determined by means of an enthalpy titration of ≈ 5 mM NaOH, prepared by electrolysis, with 0.1 M HClO$_4$. The value obtained was 13.05 ± 0.03 kcal/mole, neglecting the probably very small dilution effects. From the value of log $K_w = -14.22$ in 3 M NaClO$_4$,[7] we obtain $\Delta G° = 19.40$ kcal/mole.

Combining the data for the hydrolysis of Cu(II) with the thermochemical data for the ionisation of water in 3 M NaClO$_4$ medium

	$\Delta G°$, kcal	$\Delta H°$, kcal	$\Delta S°$, e.u.
$H_2O \rightleftharpoons H^+ + OH^-$	19.40	13.05	-21.3
we obtain			
$2Cu^{2+} + 2\,OH^- \rightleftharpoons Cu_2(OH)_2^{2+}$	-24.3	-10.3	$+47$

The enthalpy change for the mononuclear step

$$Cu^{2+} + H_2O \rightleftharpoons CuOH^+ + H^+ \quad (\log \beta_{11} \approx -8,\ \Delta G° \approx 10.9 \text{ kcal/mole})$$
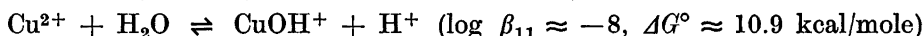
may be estimated under the assumption that the entropy change is negligible or slightly positive, as for the formation of Cu$_2$(OH)$_2^{2+}$, an assumption which does not seem unreasonable. The estimated value will then be $\Delta H_{11} = 11-12$ kcal/mole.

The thermochemical data for the Cu(II) hydrolysis will be discussed in a forthcoming paper in connection with a discussion of the thermochemical data for the hydrolysis of some other cations.

REFERENCES

1. Berecki-Biedermann, C. *Arkiv Kemi* 9 (1956) 175.
2. Pedersen, K. J. *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* 20 (1943) No. 7.
3. Arnek, R. and Kakolowicz, W. *Acta Chem. Scand.* 21 (1967) 1449.
4. Biedermann, G. and Othaki, H. *Personal communication.*
5. Sillén, L. G. *Acta Chem. Scand.* 18 (1964) 1085.
6. Ingri, N. and Sillén, L. G. *Arkiv Kemi* 23 (1964) 97.
7. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. *Acta Chem. Scand.* 11 (1957) 1034.