

Thermochemical Studies of Hydrolytic Reactions

7. A Recalculation of Calorimeter Data on Iron(III) Hydrolysis

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The calorimeter data, reported in 1962 by one of the authors (K.S.), on iron(III) hydrolysis in the medium 3 M NaClO₄ at 25°C have been recalculated by means of the computer program LETAGROPVRID. The following results were obtained (deviations 3σ):

	ΔH° , kcal	ΔS° , e.u.
$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}^+$	11.0 ± 1.8	23 ± 6
$2 \text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	10.0 ± 0.4	20.0 ± 1.3
$3 \text{Fe}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	14.3 ± 2.1	22 ± 7

In 1957 and 1959 some enthalpy titrations were made in this Department on hydrolysed iron(III) perchlorate solutions in the medium 3 M (Na)ClO₄ at 25°C,¹ using a calorimeter constructed.² Hydrolysed solutions, in the concentration range 5–100 mM Fe(III) total, were titrated with perchloric acid from a thermostated buret. By means of the equilibrium constants given by Hedström³ and Biedermann⁴ for the formation of the hydrolytic species, the concentrations of the complexes were first calculated. By successive approximations, and with graphical methods the enthalpies of the complexes and the analytical hydrogen excess, H_0 , in the initial solutions were then determined. It was thought worthwhile to treat the data again using the computer program LETAGROPVRID.^{5,6}

Two series of enthalpy titrations were carried out: series A (Nov. 1957–Jan. 1958) and series B (June 1959). As there was some evidence for the presence of colloidal iron(III) hydroxide in the series A titrations the titrations were repeated (series B) at so large values of H_0 that the formation of colloidal iron(III) hydroxide particles need not be feared. Only the data from the series B titrations have been treated in this recalculation.

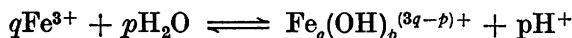
THE LETAGROPVRID TREATMENT

By means of the computer program LETAGROPVRID, a generalised least squares method, it is possible to rapidly find that combination of H_0 and the enthalpies, ΔH , which minimizes the error square sum:

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

Q is the heat effect. The computer also finds the standard deviations for the constants and the standard deviation for the measured quantity, σ_Q .

We write $\beta_{p,q}$ for the equilibrium constant and $\Delta H_{p,q}$ for the enthalpy change of



The formulas and equilibrium constants of the complexes in the medium 3 M NaClO₄ at 25°C have been determined by Hedström³ and later by Biedermann.⁴ Hedström explained his data by assuming the complexes $\text{Fe}_q(\text{OH})_p^{(3q-p)+}$ with the (p,q) values (1,1), (2,1), and (2,2) and the equilibrium constants $\beta_{1,1} = 9.0 \times 10^{-3}$ M, $\beta_{2,1} = 4.9 \times 10^{-7}$ M², and $\beta_{2,2} = 1.22 \times 10^{-3}$ M. Biedermann explained his data by adding one more complex, with the (p,q) value (4,3), to those previously suggested by Hedström and gave the equilibrium constants $\beta_{1,1} = 9.0 \times 10^{-4}$ M, $\beta_{2,1} = 4.9 \times 10^{-7}$ M², $\beta_{2,2} = 1.10 \times 10^{-3}$ M and $\beta_{4,3} = 1.7 \times 10^{-6}$ M².

Table 1. Results of LETAGROPVRID treatment.

a) Species: $\text{Fe}_2(\text{OH})_2^{4+}$ and FeOH^{2+} .

Calculation:	I ^a	II ^b	III	IV	V
ΔH_{22} , kcal/mole	9.68 ± 0.19	9.72 ± 0.15	9.97 ± 0.12	9.92 ± 0.04	10.40 ± 0.06
ΔH_{11} , kcal/mole	12.1 ± 0.7	12.2 ± 0.7	11.0 ± 0.6	11.4 ± 0.9	—
$10^3 \beta_{22}$	1.22	1.22	1.22	1.21 ± 0.03	1.62 ± 0.04
$10^4 \beta_{11}$	9.0	9.0	9.0	8.9 ± 0.8	—
σ_Q , cal	0.032	0.074	0.057	0.057	0.070

^a $\text{Fe(III)}_{\text{tot}} \leq 50$ mM;

^b $\delta H_0 = 0$

b) Species: $\text{Fe}_2(\text{OH})_2^{4+}$, FeOH^{2+} , and $\text{Fe}_3(\text{OH})_4^{5+}$;

$$\beta_{22} = 1.10 \times 10^{-3}, \beta_{11} = 9.0 \times 10^{-4}, \beta_{43} = 1.7 \times 10^{-6}$$

Calculation:	VI	VII
ΔH_{22} , kcal/mole	8.4 ± 0.4	9.97 ± 0.13
ΔH_{11} , kcal/mole	15.0 ± 0.9	11 n.v. ^c
ΔH_{43} , kcal/mole	17.8 ± 1.0	14.3 ± 0.7
σ_Q , cal	0.057	0.059

^c not varied

In the LETAGROPVRID calculations the enthalpies, $\Delta H_{p,q}$, and the analytical errors, δH_0 , were treated as unknown independent parameters; in some cases the equilibrium constants, $\beta_{p,q}$, were also considered unknown. The results of the LETAGROPVRID treatment are summarized in Table 1. The deviations given in this table are σ , the standard deviation calculated by LETAGROPVRID.

DISCUSSION

The main hydrolysis product of iron(III) is the dinuclear species $\text{Fe}_2(\text{OH})_2^{4+}$. The species FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_3(\text{OH})_4^{5+}$ represent only a small fraction of the hydrolysis products. The species $\text{Fe}(\text{OH})_2^+$ has been neglected in the following; calculations showed that it is of no importance for the interpretation of the heat data.

The results of the calculations when the species $\text{Fe}_2(\text{OH})_2^{4+}$ and FeOH^{2+} with Hedström's equilibrium constants were considered, are summarized in Table 1a. In the first calculation only the data with $\text{Fe}(\text{III})_{\text{total}} \leq 50$ mM was treated; the upper limit of $\text{Fe}(\text{III})_{\text{total}}$ studied by Hedström was 50 mM. In the following calculations the complete data set was used. In calculation II the systematic errors δH_0 were assumed to be 0, whereas in the other calculations they were variable parameters to be determined. Obviously a considerable improvement was obtained by introducing the δH_0 . The δH_0 obtained in the different calculations agreed within the limits of error; the δH_0 from calculation II are given in Table 2 with their standard deviations.

Table 2. Analytical errors, δH_0 .

Experiment	1a, b	2a, b	3a, b	4a, b	5a, b	6
δH_0 , mM (LETAGROP- VRID)	0.5 ± 0.3	-0.9 ± 0.5	-0.1 ± 0.2	0.6 ± 0.3	0.7 ± 0.7	-2.5 ± 0.4
	1.2 ± 0.3	-1.1 ± 0.5	-0.4 ± 0.1	-0.5 ± 0.2	-0.2 ± 0.6	
δH_0 , mM (Schlyter, 1962, Ref. 2)	-1.7	-3.9	-2.1	+2.6	+3.0	-0.6

In calculation IV β_{22} and β_{11} were also treated as unknown; the $\beta_{p,q}$ obtained agreed with Hedström's values. In calculation V FeOH^{2+} was neglected. This gave a decidedly worse fit.

The results of the calculations considering, in addition to $\text{Fe}_2(\text{OH})_2^{4+}$ and FeOH^{2+} , $\text{Fe}_3(\text{OH})_4^{5+}$ with Biedermann's equilibrium constants are given in Table 1b. In calculation VI all three enthalpies were treated as unknown. In calculation VII ΔH_{11} was kept constant at 11 kcal. As can be seen there is a strong coupling between ΔH_{22} , ΔH_{11} , and ΔH_{43} . The concentration range of the calorimeter data, $\text{Fe}(\text{III})_{\text{tot}} \leq 100$ mM, is not very favourable for the determination of ΔH_{43} . In our opinion a value for $\Delta H_{11} = 11$ kcal/mole is

more reasonable than $\Delta H_{11} = 15$ kcal/mole, obtained in calculation VI. Milburn⁷ obtained $\Delta H_{11} = 10.2 \pm 0.3$ kcal/mole from the temperature coefficient between 18° and 32°C of spectrophotometric data in the medium 1 M (NaClO₄). Wells⁸ has pointed out that the heat of dissociation of the first proton for the tripositive ions in the first transition series (with the exception of Mn³⁺) seems to be roughly the same ≈ 10 kcal/mole. Further a value $\Delta H_{11} = 11$ kcal/mole is consistent with the assumption that the bond Fe—OH in FeOH²⁺ has some covalent character; this is indicated by the very large value of K for the formation of FeOH²⁺. The LETAGROPVRID calculations in Table 1 and the considerations above lead us to suggest the following ΔH_{pq} and ΔS_{pq} values (with 3σ):

$$\begin{array}{ll} \Delta H_{11} = 11.0 \pm 1.8 \text{ kcal/mole} & \Delta S_{11} = 23 \pm 6 \text{ e.u.} \\ \Delta H_{22} = 10.0 \pm 0.4 \text{ kcal/mole} & \Delta S_{22} = 20.0 \pm 1.3 \text{ e.u.} \\ \Delta H_{43} = 14.3 \pm 2.1 \text{ kcal/mole} & \Delta S_{43} = 22 \pm 7 \text{ e.u.} \end{array}$$

The discrepancy between the values reported in 1962 and those obtained with LETAGROPVRID is, in our opinion, mainly due to the fact that enormous difficulties are met in treating a system of such complexity as iron(III) hydrolysis using graphical methods. In addition the data from both the series A and series B measurements were calculated together, whereas the present recalculation was performed with data from only the series B measurements.

Finally it must be emphasized that there seems to need for both more accurate calorimeter work and emf work on iron(III) hydrolysis (the accuracy could probably be improved by modern techniques) to obtain more reliable thermodynamic data.

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