

# The Hydrolysis of Iron in Methanol Solutions

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## Summary

The method of Siddall and Vosburgh (8) has been used for determining the first hydrolysis constant of iron (III) ion in a 20% water 80% methanol solvent in the presence of nitrate salts. Optical densities of a series of solutions of known variable acidity were made at temperatures ranging from 20 to  $-60^{\circ}\text{C}$  at iron concentrations of .00116 and .000272M and ionic strengths of approximately 0.15. The heat of reaction has also been calculated.

## Introduction

Many determinations have been made of the hydrolysis constant for the ferric ion in aqueous solutions (1, 3, 5-8). Little if anything has been done in nonaqueous solutions, however. In the course of an experiment involving reaction kinetics for the formation of the iron thiocyanate complex it became necessary to determine the hydrolysis constant in a 20% water 80% methanol solvent at temperatures down to  $-60^{\circ}\text{C}$ .

## Experimental

A stock solution of ferric nitrate of 0.0290M. was made in anhydrous methanol. Dilutions from this stock were made for the experimental runs. The ionic strength of the solution was adjusted to approximately 0.15 with an aqueous solution of sodium nitrate. The pH was adjusted with 6N. nitric acid. Distilled water was added so that the final solution was 20% water.

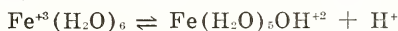
Absorbancy was measured with a Bausch and Lomb model 20 spectrophotometer at 355  $m\mu$ . pH measurements were made on a Beckman Zeromatic pH meter using a glass electrode and a calomel reference cell.

Bacarella (2) and others have verified that pH determinations made with the glass electrode are correct in a water-methanol system. However as an added check methanol-water blanks were adjusted on the pH meter to the same value as the iron solutions. These blanks were then titrated with standard sodium hydroxide to determine the concentration of the hydrogen ion.

The cold temperatures were maintained in a dry ice and methanol bath. A tube with an insulating vacuum jacket was used to contain the cold iron solutions during the measurement of absorbance. The per cent transmittance was read and converted to absorbance.

## Results and Interpretation

The first hydrolysis of the ferric may be written



The hydrolysis constant ( $K_h$ ) is therefore

$$K_h = \frac{[\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{+2}][\text{H}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{+3}]} \quad (1)$$

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If

- [Fe]<sup>°</sup> = total iron concentration  
 A = the absorbance  
 b = cell length  
 a = the molar absorbancy index of Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>+2</sup>

$$\text{then} \quad A = ab[\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{+2}] \quad (2)$$

Substituting the value of [Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>+2</sup>] from equation (1) into equation (2) we have

$$\frac{A[\text{H}^+]}{ab} = K_h[\text{Fe}(\text{H}_2\text{O})_6^{+3}] \quad (3)$$

It is assumed that [Fe]<sup>°</sup> = [Fe(H<sub>2</sub>O)<sub>6</sub><sup>+3</sup>] + [Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>+2</sup>]

$$\text{Then} \quad \frac{A[\text{H}^+]}{ab} = K_h \{ [\text{Fe}]^\circ - [\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{+2}] \} \quad (4)$$

$$\text{and} \quad A[\text{H}^+] = abK_h[\text{Fe}]^\circ - \frac{abK_hA}{ab} \quad (5)$$

$$\text{this yields} \quad A \{ [\text{H}^+] + K_h \} = abK_h[\text{Fe}]^\circ \quad (6)$$

Rearranging equation (6) we have

$$\frac{1}{A} = \frac{1}{(abK_h[\text{Fe}]^\circ)} [\text{H}^+] + \frac{1}{ab[\text{Fe}]^\circ} \quad (7)$$

Therefore a plot of 1/A versus [H<sup>+</sup>] should give a straight line with slope  $m = 1/abK_h[\text{Fe}]^\circ$  and intercept  $y_0 = 1/ab[\text{Fe}]^\circ$ .

At 355 mμ the absorbancy is due to the first hydrolysis product (7, 8) Fe(H<sub>2</sub>O)<sub>5</sub>OH<sup>+2</sup>, therefore absorbancy was measured for a series of iron solutions of constant concentration and ionic strength but varying concentrations of hydrogen ion and temperature. The reciprocals of A were plotted against the concentration of hydrogen ion. From equation (7) it can be seen that  $K_h = y_0/m$ . Values of  $y_0$  and  $m$  were taken from the plots and values of  $K_h$  calculated.

Table 1a shows the dependence of the absorbance upon the hydrogen ion concentration. Table 1b gives the relation between the hydrolysis constant and the temperature.

Table 1a		Table 1b	
[H <sup>+</sup> ] M.	Absorbance	Temperature C°	K <sub>h</sub>
0.139	0.0269	-59.2	0.00327 ± 0.000820
0.0996	0.0410	-49.7	0.00352 ± 0.00248
0.0587	0.0562	-41.8	0.00817 ± 0.00292
0.0437	0.0670	-25.0	0.00922 ± 0.00508
0.0127	0.142	0.0	0.0322 ± 0.0122
0.00950	0.155	20.0	0.0365 ± 0.00350
0.00184	0.346		
0.00147	0.366		

The absorbancy of iron solutions of varying hydrogen ion concentration is shown in table 1a for -50°C. Similar series of runs were made at temperatures of -60, -40, -25, 0, and 20°C. On the assumption of a linear relationship the values of  $K_h$  were calculated. A plot of 1/A versus

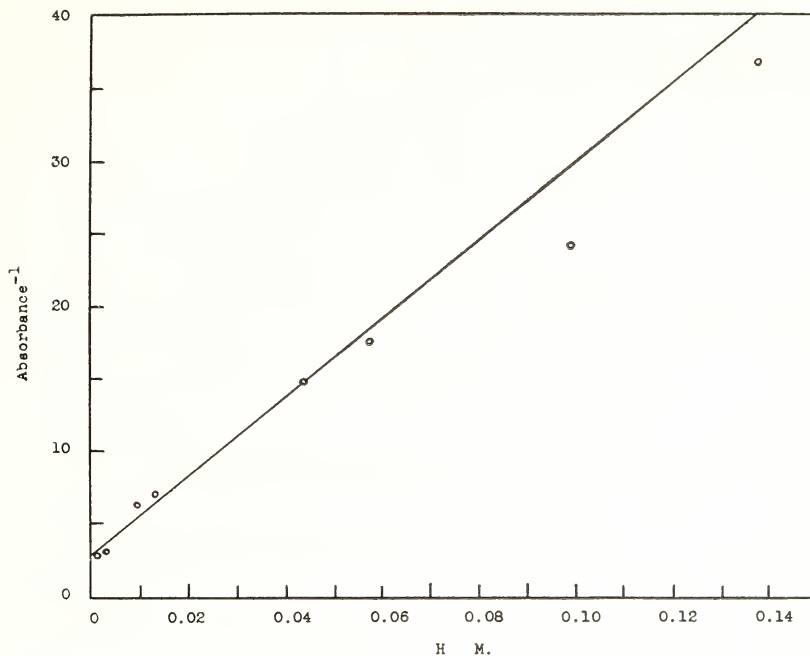


Fig. 1. The relation between absorbance<sup>-1</sup> and the molar concentration of the hydrogen ion at -50°C.

[H<sup>+</sup>] is shown in figure 1 for -50°C. The values of K<sub>b</sub> at various temperatures are shown in table 1b.

The heat of reaction may be obtained by plotting -logK<sub>b</sub> versus T<sup>-1</sup>,

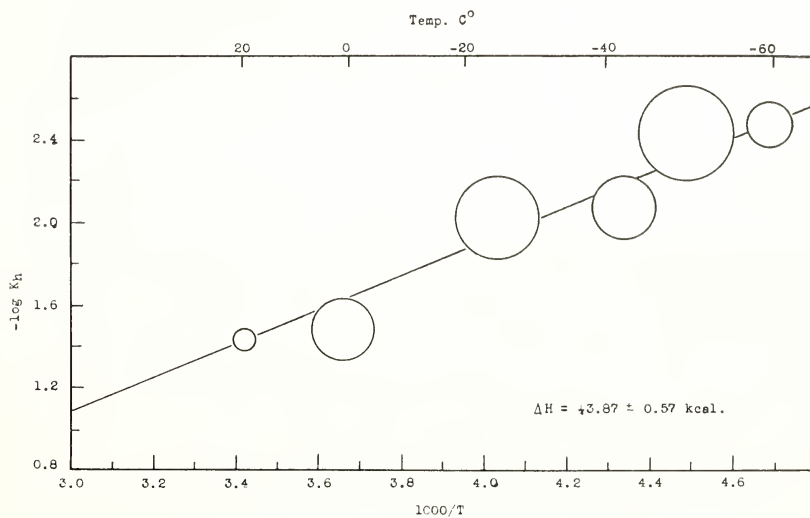


Fig. 2. Relation between the values of K<sub>b</sub> and temperature.

where T is the absolute temperature of the reaction. The heat of reaction  $\Delta H$  can be calculated from the slope of the line as follows:

$$\Delta H = +\text{slope} \times 2.303R$$

where R is the ideal gas constant, 1.987 cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Figure 2 graphically presents this information. The slope of the curve predicts the heat of reaction to be  $+3.87 \pm 0.57$  kcal.

No attempts were made to study the effects of dimerization of the iron. This may well be a factor in solutions of relatively low dielectric constant but there is evidence (1, 6, 7) against the formation of polynuclear species in relatively dilute solutions of iron.

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