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STABILITY OF FERROUS SULFAMATE
IN NITRIC ACID SOLUTIONS

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ABSTRACT

The rates of oxidation of ferrous ion in solutions of sulfamic acid and 5.0 to 7.0M HNO_3 were measured at temperatures of 23 to 55°C. From these rates, an expression, $\log k = 4.56 \log [\text{HNO}_3] - 5140(1/T^\circ\text{K}) + 10.4$, was derived for calculating the rate of oxidation of ferrous ion under these conditions.

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INTRODUCTION

Ferrous sulfamate is used to adjust or control the valence states of plutonium and neptunium in nitrate solutions.⁽¹⁾ In some applications a suitable concentration of ferrous sulfamate must be maintained for an extended period during a chemical operation. For such applications a reliable prediction is needed for the rate at which ferrous sulfamate is destroyed in the process solution.

The stability of ferrous sulfamate in specific process solutions has been studied previously.^(2,3) The present study was made to provide data for predicting the rate of oxidation of ferrous ion in solutions of sulfamic and nitric acids.

DISCUSSION

When ferrous sulfamate is used to control valence states in nitric acid solutions, the ferrous ion serves as the reductant, while the sulfamate ion reacts with nitrite to prevent the rapid (autocatalytic) oxidation of ferrous and other ions. However, in the presence of sulfamic acid, nitric acid oxidizes ferrous ion at a measurable rate.⁽⁴⁾ The important reactions involved in the oxidation are:

At lower temperatures and acid concentrations, oxidation is predominately by Reaction 1, because Reaction 2 reduces the concentration of HNO_2 and thereby inhibits Reaction 3.

The rate of oxidation of ferrous ion was measured as a function of temperature and of the concentrations of nitric acid, ferrous sulfamate, and free sulfamic acid. In the experimental procedure, an aliquot of ferrous sulfamate was

added to the appropriate solution at the desired temperature, and the concentration of ferrous ion was determined at regular intervals by ceric titration.

The oxidation of ferrous sulfamate in nitric acid solution was first order with respect to the ferrous ion for acid concentrations of 5.0 to 8.0M and temperatures of 23 to 42°C. As shown in Figure 1, the first-order rate constant was about the same for 0.05M and 0.15M ferrous sulfamate in 8.0M HNO₃ at 42°C. The oxidation at 55°C was first order for 5 to 7M HNO₃, but for 8M HNO₃ at this temperature, the rate increased with time. However, as shown in Figure 2, the addition of sulfamic acid to increase the ratio of sulfamate to ferrous restored the oxidation to a first-order rate.

Data showing the effect of nitric acid concentration on the oxidation rates at 30 and 34°C are presented in Figure 3. Average data for temperatures of 23 to 42°C gave a rate dependent on the 4.56 power of the acid concentration.

The effect of temperature on the oxidation rate is shown in Figure 4. These data were used to calculate an apparent activation energy of 23.5 kcal/mol for the reaction.

Results from 23 rate experiments were treated by the method of least squares, and the oxidation of ferrous ion by nitric acid was fitted by the expression

$$\log k = 4.56 \log [\text{HNO}_3] - 5140 \left(\frac{1}{T^\circ\text{K}} \right) + 10.4$$

where k is the first-order rate constant for the oxidation of ferrous ion. The agreement between the calculated and experimental rate constants is shown in Table I. The oxidation of ferrous sulfamate in 8M HNO₃ at 55°C does not fit the empirical expression. However, under these conditions the oxidation is so rapid ($t_{\frac{1}{2}} = 6$ minutes), that a prediction of the rate is unnecessary.

FIG. 1 EFFECT OF CONCENTRATION OF FERROUS SULFAMATE ON RATE OF OXIDATION OF FERROUS ION

FIG. 2 EFFECT OF CONCENTRATION OF SULFAMIC ACID ON RATE OF OXIDATION OF FERROUS ION

FIG. 3 EFFECT OF CONCENTRATION OF NITRIC ACID ON RATE OF OXIDATION OF FERROUS ION

FIG. 4 EFFECT OF TEMPERATURE ON RATE OF OXIDATION OF FERROUS ION

TABLE I

Experimental and Calculated Rates of Oxidation of Ferrous Ion
in Solutions of Sulfamic and Nitric Acids

HNO ₃ Conc, M	Temp, °C	Oxidation Rate, min ⁻¹		Difference, %
		Experimental	Calculated	
5.0	23	0.00016	0.00016	-
6.0	23	0.00035	0.00037	5.4
7.0	23	0.00066	0.00074	10.8
8.0	23	0.0014	0.0014	-
5.0	30	0.00049	0.00041	22.0
6.0	30	0.00081	0.00095	14.7
7.0	30	0.0017	0.0019	10.5
8.0	30	0.0036	0.0035	2.9
5.0	34	0.00065	0.00066	1.5
6.0	34	0.0014	0.0015	6.7
7.0	34	0.0028	0.0031	9.7
8.0	34	0.0059	0.0056	5.4
5.0	38	0.0013	0.0011	18.2
6.0	38	0.0026	0.0024	8.3
7.0	38	0.0049	0.0049	-
8.0	38	0.0105	0.0091	15.4
5.0	42	0.0019	0.0019	-
6.0	42	0.0043	0.0044	2.3
7.0	42	0.0084	0.0089	5.6
8.0	42	0.0181	0.0160	13.1
5.0	55	0.0055	0.0079	30.3
6.0	55	0.0196	0.0180	8.9
7.0	55	0.0410	0.0370	10.8

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