Key for Kinetics of Oxidation of Fe(II) to Fe(III)

Part I: pH > 3.5

The data for Part I is an example of the initial rate method for finding a rate law. The key to working with data of this sort is to isolate pairs of experiments in which the concentration of only one species is changing.

- To find the reaction order for Fe^{2+} we compare experiments 1 and 2, finding that doubling its concentration results in a doubling of the rate; thus, the rate is first-order in Fe^{2+}.
- To find the reaction order for O_2 we compare experiments 2 and 4, finding that increasing the partial pressure by 50% leads to a 50% increase in the rate; thus, the rate is first-order in O_2.
- To find the reaction order for H_3O^+ we compare experiments 1 and 3, finding that increasing its concentration by a factor of 10 causes the rate to decrease by a factor of 100; thus, the rate is inverse second-order in H_3O^+. Yes, sometimes a species can slow a reaction down.

At this point we know that the rate law is

$$R = k_1[Fe^{2+}][H_3O^+]^{-2}P_{O_2}$$

To find the rate constant we substitute concentrations, partial pressures, and rates from each experiment into the rate law and solve for k_1. Doing this for each experiment produces the same result of 1.2×10^{-11} M^2 atm^{-1} d^{-1}. Pay particular attention to the units and convince yourself that they are correct.

To rewrite the rate law in terms of OH^- we note that

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

Solving this equation for $[H_3O^+]$ and substituting back into our rate law gives

$$R = k_1 Kw^{-2}[Fe^{2+}][OH^-]^2 P_{O_2} = [Fe^{2+}][OH^-]^2 P_{O_2}$$

The value for k_2, therefore, is k_1/K_w^2, or 1.2×10^{17} M^{-2} atm^{-1} d^{-1}. Again, be sure to convince yourself that the units are correct.

Part II: pH < 3.5

To show that the data are indeed first-order we estimate the first several half-lives and observe their pattern. The first three half-lives are approximately 29,000 d each, which is consistent with the observation that the half-life for a first-order process is independent of concentration.

Knowing the half-life allows us to calculate the pseudo-order rate constant, k_4; this is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{29000 \text{ d}} = 2.4 \times 10^{-5} \text{ d}^{-1}$$

This, in turn, allows us to calculate k_3 since

$$k_4 = k_3 P_{O_2}$$

Thus

$$k_3 = k_4/P_{O_2} = 2.4 \times 10^{-5} \text{ d}^{-1}/0.20 \text{ atm} = 1.2 \times 10^{-4} \text{ d}^{-1} \text{ atm}^{-1}$$

Finally, at a pH of 3.0 and a partial pressure of 0.20 atm a 4.7 mM solution of Fe^{2+} will follow the pseudo-order kinetics given by the rate law

$$R = k_4[Fe^{2+}]$$

For a first-order reaction we know that

$$\ln[Fe^{2+}]_t = \ln[Fe^{2+}]_0 - kt$$

Thus

$$\ln(1.2 \text{ mM}) = \ln(4.7 \text{ mM}) - (2.4 \times 10^{-5} \text{ d}^{-1})t$$

$$t = 56,900 \text{ d}$$

Note that the we can leave the concentrations in mM if we prefer.

Part III: Combining the Rate Laws

To find the pH where the two mechanisms for the oxidation of Fe^{2+} have the same rate we first set them equal to each other

$$k_1[Fe^{2+}][H_3O^+]^{-2}P_{O_2}^\gamma = k_3[Fe^{2+}]P_{O_2}$$
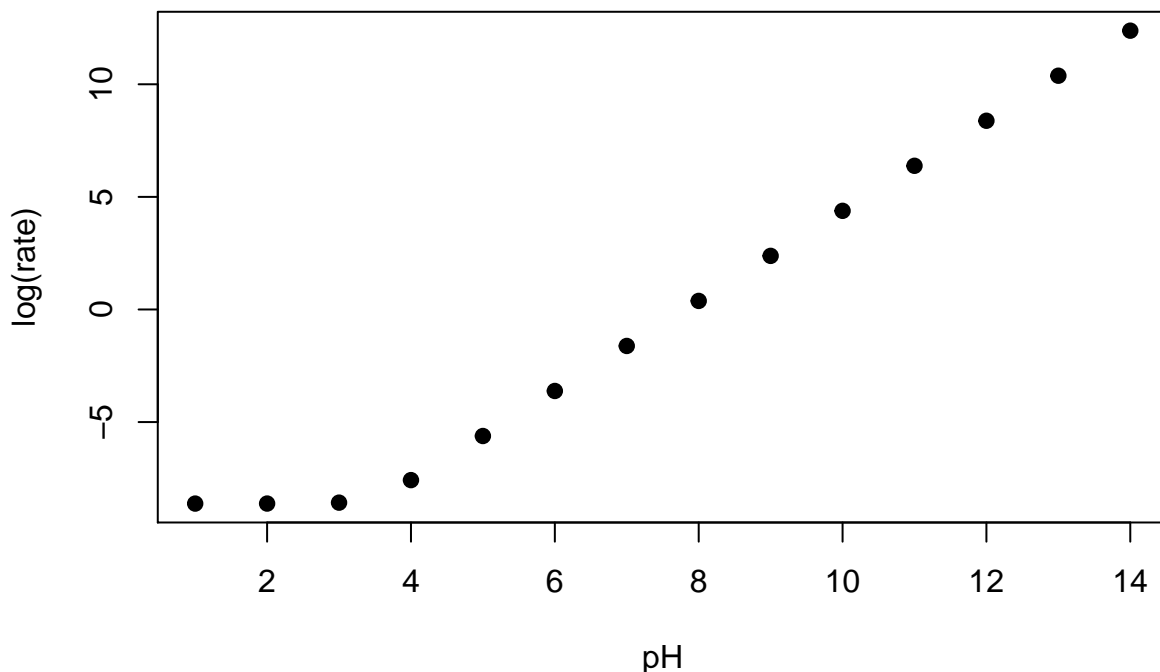
and then simplify, giving

$$k_1[H_3O^+]^{-2} = k_3$$

Next, we solve this for the concentration of H_3O^+

$$[H_3O^+] = \sqrt{\frac{k_1}{k_3}} = \sqrt{\frac{1.2 \times 10^{-11} \text{ M}^2\text{atm}^{-1}\text{d}^{-1}}{1.2 \times 10^{-4} \text{ atm}^{-1}\text{d}^{-1}}} = 3.16 \times 10^{-4} \text{ M}$$

which corresponds to a pH of 3.5.

A graph of log(rate) vs. pH is shown here

Note that the rate remains constant until the pH is greater than 3 and then it starts to increase quickly. Clearly the rate of oxidation is favored at more basic pH levels. The reason for this is the formation of various Fe^{2+}–OH^- complexes. It turns out that the oxidation of Fe^{2+} is much easier when the iron is complexed with hydroxide. There are important environmental implications for this oxidation process. Ground water percolating through gob piles from strip mining is often fairly acidic and somewhat anaerobic (low in O_2), conditions that favor the presence of Fe^{2+}. When the water seeps into the open and mixes with other water, the pH increases and, with the presence of atmospheric O_2, the Fe^{2+} quickly oxidizes to Fe^{3+}, which precipitates as $Fe(OH)_3$ because iron(III)hydroxide is much less soluble than iron(II)hydroxide. If you have ever encountered standing water that has an orange gunky looking precipitate, then you have seen the result of this process!