

Kinetics of the Oxidation of Fe²⁺ to Fe³⁺

The ferrous ion, Fe²⁺, oxidizes to ferric ion, Fe³⁺, in the presence of atmospheric oxygen. The rate law for this reaction is pH-dependent, following one apparent rate law when the pH is greater than 3.5 and a different apparent rate law when the pH is below 3.5.

Part I – pH > 3.5. The following initial rates (defined as -d[Fe²⁺]/dt) are for solutions buffered to pH levels greater than 3.5.

[Fe ²⁺] (M)	pH	P _{O₂} (atm)	Rate (M/day)
1.0×10 ⁻⁴	5.0	0.20	2.4×10 ⁻⁶
2.0×10 ⁻⁴	5.0	0.20	4.8×10 ⁻⁶
1.0×10 ⁻⁴	4.0	0.20	2.4×10 ⁻⁸
2.0×10 ⁻⁴	5.0	0.30	7.2×10 ⁻⁶

Using this data, determine the reaction orders and rate constant (with appropriate units) for the rate law

$$\text{Rate} = k_1[\text{Fe}^{2+}]^\alpha[\text{H}_3\text{O}^+]^\beta\text{P}_{\text{O}_2}^\gamma$$

Sometimes it is desirable to write this rate law in terms of [OH⁻] instead of [H₃O⁺]. Knowing that

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

rewrite the rate law (and find the new rate constant) so that it is expressed as

$$\text{Rate} = k_2[\text{Fe}^{2+}]^\alpha[\text{OH}^-]^\delta\text{P}_{\text{O}_2}^\gamma$$

Part II – pH < 3.5. Interestingly, at pH levels less than 3, the concentration of H₃O⁺ does not affect the reaction's rate. Under these conditions the rate law is

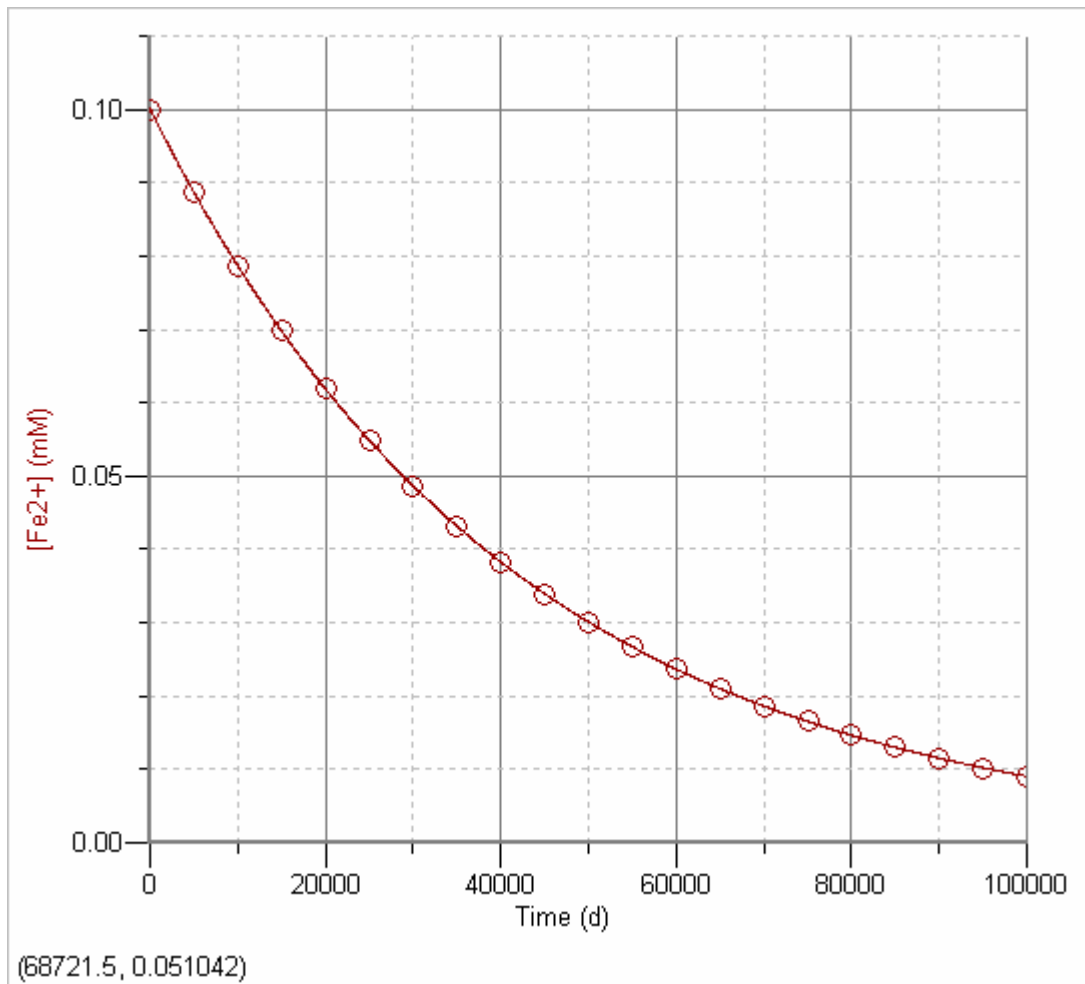
$$\text{Rate} = k_3[\text{Fe}^{2+}]\text{P}_{\text{O}_2}$$

The data shown on the next page gives concentrations of Fe²⁺ as a function of time under pseudo-order conditions (P_{O₂} = 0.2 atm) for which the rate law is

$$\text{Rate} = k_4[\text{Fe}^{2+}]$$

Estimate the first 3 or 4 half-lives and explain why these results support the rate law given above. Based on these results determine the rate constants k₄ and k₃. At a pH of

3.0 and a partial pressure of O₂ of 0.20 atm, how long will it take for the concentration of Fe²⁺ to decrease from an initial concentration of 4.7 mM to 1.2 mM?



Part III – Combining the Rate Laws. The actual rate law for the oxidation of Fe²⁺ is the summation of the rate laws determined under different pH conditions

$$\text{Rate} = k_1[\text{Fe}^{2+}]^\alpha[\text{H}_3\text{O}^+]^\beta\text{P}_{\text{O}_2}^\gamma + k_3[\text{Fe}^{2+}]\text{P}_{\text{O}_2}$$

Find the pH where $k_1[\text{Fe}^{2+}]^\alpha[\text{H}_3\text{O}^+]^\beta\text{P}_{\text{O}_2}^\gamma$ is equal to $k_3[\text{Fe}^{2+}]\text{P}_{\text{O}_2}$ and comment on the significance of this result. Suppose that the initial concentration of Fe²⁺ is 1.0×10^{-4} M and that the partial pressure of O₂ is 0.2 atm. Calculate and graph the reaction's rate for pH levels ranging from 1 to 14; your graph will be easier to examine if you plot log(rate) vs. pH. What does this graph tell you about the conditions favoring the oxidation of Fe²⁺? Can you propose an explanation for why the rate law is so much faster above a critical pH?