The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O\textsubscript{2} in aqueous solution – basic principles and a simple heuristic description

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Abstract

The spontaneous chemical oxidation of Fe(II) to Fe(III) by O\textsubscript{2} is a complex process involving meta-stable partially oxidized intermediate species such as green rusts, which ultimately transform into a variety of stable iron oxide end-products such as hematite, magnetite, goethite and lepidocrocite. Although in many practical situations the nature of the end-products is of less interest than the oxidation kinetics, it is difficult to find in the literature a description of all the basic steps and principles governing the kinetics of these reactions. This paper uses basic aquatic-chemistry equilibrium theory as the framework upon which to present a heuristic model of the oxidation kinetics of Fe(II) species to ferric iron by O\textsubscript{2}. The oxidation rate can be described by the equation (in units of mol Fe(II)/(l min)):

\[
\frac{d[\text{Fe}^{2+}]}{dt} = \frac{6 	imes 10^{-7}}{C_0^{1/2}} \left[ \text{Fe}^{2+} \right] + 1.7 \left[ \text{Fe(OH)}^+ \right] + 4.3 \times 10^{5} \left[ \text{Fe(OH)}_2^+ \right].
\]

This rate equation yields a sigmoid-shaped curve as a function of pH; at pH values below \( \approx 5 \), \left[ \text{Fe(OH)}_2^+ \right] dominates and the rate is independent of pH. At pH > \( \approx 5 \), \( \left[ \text{Fe(OH)}_2^+ \right] \) determines the rate because it is far more readily oxidized than both \text{Fe}^{2+} \) and \text{FeOH}^+. Between pH 5 and 8 the \text{Fe(OH)}_2^+ concentration rises steeply with pH and the overall oxidation rate increases accordingly. At pH values > \( \approx 8 \), \left[ \text{Fe(OH)}_2^+ \right] no longer varies with pH and the oxidation rate is again independent of pH. The paper presents a heuristic overview of the pH dependent kinetics of aqueous ferrous oxidation by O\textsubscript{2(aq)} which we believe will be useful to professionals at both research and technical levels.

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1. Introduction

Ferrous (Fe\textsuperscript{2+}) and ferric (Fe\textsuperscript{3+}) ions in aqueous solution occur in a wide variety of commonly encountered aquatic contexts such as incidents of “red water” in water distribution systems, acid mine drainage problems, a diverse range of industrial water treatment processes and natural cycles in fresh and marine water environments. The spontaneous chemical oxidation of ferrous to ferric by O\textsubscript{2} is a complex process involving a variety of partially oxidized meta-stable ferrous–ferric intermediate species (e.g. green rusts) which are difficult to characterise or predict. These Fe-intermediates ultimately transform into a variety of stable iron oxide end-products such as hematite, magnetite, goethite and lepidocrocite. The exact end-product(s) formed depends upon environmental conditions chief among which are pH, temperature, solution composition and oxidation rate. Yet in many practical situations the nature of the end-products is of less interest than the oxidation kinetics which are primarily independent of the final iron oxide species formed. This paper presents a heuristic overview of the kinetics of aqueous ferrous oxidation by O\textsubscript{2(aq)} which we believe is a valuable synthesis of an old, dispersed and somewhat forgotten literature that is nonetheless increasingly relevant in a great number of practical situations encountered today.
The theory underlying the kinetics of oxidation of Fe(II) in aqueous solution begins with a consideration of empirical observations of the rate in relation to pH. Stumm and Morgan (1996) present the following kinetic equation for the oxidation of Fe²⁺ to Fe³⁺ with O₂(aq) as the electron acceptor:

\[
\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}][OH^-]^2P_{O_2}
\]  

(1)

This empirical equation was derived by curve fitting techniques from data attained from the oxidation of ferrous solutions of no more than 0.5 mM/l (~28 mg Fe/l), and at pH values between ~4 and 6. In Fig. 1 it can be seen that below pH ~4 the rate of oxidation becomes very low, and is fundamentally independent of pH. Millero (1985) also presented data for the rate of oxidation of Fe(II) in solution which, among other observations, includes observations at pH values higher than 6 (Fig. 2). Millero’s results indicate that at pH values greater than ~8 the rate of ferrous oxidation (these data were obtained from seawater but the author extrapolated it to freshwater) is also independent of pH. At pH values lower than ~8, Millero’s results are in agreement with Fig. 1. Thus the overall Fe(II) oxidation rate versus pH plot shows a central region where the rate is strongly pH dependent flanked by regions on either side where the rate is principally not effected by pH. Note that in freshwater above pH 9.0 the concentration of soluble Fe(II) species is so low that it is very difficult to obtain reasonably accurate empirical kinetic data.

The trend apparent from these observations can be explained in terms of the equilibrium chemistry of Fe(II) in aqueous solution. Fig. 3 is a log species–pH diagram for Fe(II) species in single phase aqueous equilibrium (Total Fe(II) concentration = 10⁻³ M) and Fig. 4 is a log species–pH diagram for Fe(II) for a two phase, aqueous-solid equilibrium, in the absence of complexing agents for ferrous iron other than water (i.e. in the absence of Cl⁻, CO₃²⁻, SO₄²⁻, etc.). Inspection of Fig. 4 reveals that in order to reach saturation at pH values below ~8, the total Fe(II) concentration must be much higher than that used to construct Fig. 1. In other words, below pH ~8 all Fe(II) solutions are effectively non-saturated solutions. The equilibrium chemistry of Fe(II) solutions below ~pH 8 is therefore better described by Fig. 3 (single phase aqueous equilibrium) while solutions above ~pH 8 are best described by Fig. 4 (two phase aqueous-solid equilibrium), which shows the fraction of the ferrous concentration that is in the solid phase (Fe(OH)₂(s)).

![Fig. 1. Oxidation rate of ferrous iron species as a function of pH (P_{O_2} = 0.20 atm). Partially redrawn from Stumm and Morgan (1996). At low pH the oxidation rate is independent of pH, while at higher pH values (>5) the second order dependence on [OH⁻] as described by Eq. (1) is fulfilled.](image)

![Fig. 2. Rate constants for oxidation of soluble Fe(II) species in water as a function of pH (from Millero (1985) based on Stumm and Lee (1961) and Roekens and Van Grieken (1983)).](image)

![Fig. 3. Log species–pH diagram of soluble ferrous hydroxide species at infinite dilution.](image)
Once formed, the rate of oxidation of Fe(OH)$_2$(s) has been shown to be independent of pH, and dependent only on the rate of the introduction of the oxidant (typically O$_2$) into the water (Prasad and Ramanasry, 1974). The current paper focuses only on the rate of oxidation of soluble ferrous species. Note that when the carbonate system is present in concentrations exceeding about 5 × 10$^{-3}$ M, ferrous iron solubility is controlled by siderite (FeCO$_3$) rather than by Fe(OH)$_2$ and the overall Fe(II) solubility becomes much lower, e.g. at pH 8.0 the combined concentration of ferrous species is around 10$^{-4}$ lower, e.g. at pH 8.0 the combined concentration of ferrous species. Note that when the carbonate system is present in concentrations exceeding about 5 × 10$^{-3}$ M, ferrous iron solubility is controlled by siderite (FeCO$_3$) rather than by Fe(OH)$_2$ and the overall Fe(II) solubility becomes much lower, e.g. at pH 8.0 the combined concentration of ferrous species is around 10$^{-4}$ lower, e.g. at pH 8.0 the combined concentration of ferrous species.

According to Eq. (1) the oxidation rate is first order with respect to PO$_2$ and [Fe$^{2+}$] and second order for [OH$^-$]. The following rate equation given by Millero (1985) which separates the individual species found in aqueous Fe(II) solution is useful for the purposes of understanding the oxidation rate in relation to pH.

$$-\frac{d[Fe^{2+}]}{dt} = (k_0[Fe^{2+}] + k_1[Fe(OH)^+])$$

$$+ k_2[Fe(OH)^0_{2(aq)}] + k_3[Fe(OH)_3^+]\cdot DO$$

where: $k_0$, $k_1$, $k_2$ and $k_3$ are oxidation rate constants (time$^{-1}$).

In Eq. (2) the value of dissolved oxygen concentration (DO) is used instead of PO$_2$ since it is in fact DO which participates in the oxidation reaction and the DO concentration will vary for a given PO$_2$ for a variety of reasons such as temperature, ionic strength and the oxygen consumption rate of the solution (Millero et al., 1987).

In Eqs. (3)–(6) the individual species in Eq. (2) are expressed explicitly as a function of the total ferrous iron concentration (Fe(II)$_T$), pH and stability constants.

$$[Fe^{2+}] = \frac{Fe(II)_T}{1 + k_1k_w \frac{[H]^+}{K}} + k_2k_w \frac{[H]^+}{K} [Fe(OH)^+]$$

$$[Fe(OH)^+] = \frac{Fe(II)_T}{1 + k_1k_w \frac{[H]^+}{K} + k_2k_w \frac{[H]^+}{K} + k_3k_w \frac{[H]^+}{K} [Fe(OH)_3^+]$$

$$[Fe(OH)^0_{2(aq)}] = \frac{Fe(II)_T}{1 + k_1k_w \frac{[H]^+}{K} + k_2k_w \frac{[H]^+}{K} + k_3k_w \frac{[H]^+}{K} + k_4k_w \frac{[H]^+}{K} [Fe(OH)_3^+]$$

$$[Fe(OH)_3^+] = \frac{Fe(II)_T}{1 + k_1k_w \frac{[H]^+}{K} + k_2k_w \frac{[H]^+}{K} + k_3k_w \frac{[H]^+}{K} + k_4k_w \frac{[H]^+}{K} [Fe(OH)_3^+] + k_5k_w \frac{[H]^+}{K} [Fe(OH)_3^+] + k_6k_w \frac{[H]^+}{K} [Fe(OH)_3^+] + k_7k_w \frac{[H]^+}{K} [Fe(OH)_3^+]$$

where log $K_1 = 4.5$, log $K_2 = 2.93$, log $K_3 = 3.57$ (Benjamin, 2002).

Eq. (2) implies that in the course of soluble ferrous species oxidation, and in contrast with the approach presented in Eq. (1), more than one oxidation reaction occurs simultaneously (Stumm and Morgan, 1996), viz.

a. Fe$^{2+}$ → Fe$^{3+}$ + e$^-$

b. Fe(OH)$^+$ → Fe(OH)$^{2+}$ + e$^-$

c. Fe(OH)$^0_{2(aq)}$ → Fe(OH)$^+_{2(aq)}$ + e$^-$

Stumm and Morgan (1996) also provide one-electron steps for the reduction of the terminal electron acceptor, O$_2$(aq):

A. O$_2$(aq) + e$^-$ → O$_2$$_{2(aq)}$ (.$ = $ radical)

B. O$_2$$_{2(aq)}$ + e$^-$ + 2H$^+$ → H$_2$O$_2$(aq)

C. H$_2$O$_2$(aq) + e$^-$ + H$^+$ → OH$^-$$_{(aq)}$ + H$_2$O

D. OH$^-$$_{(aq)}$ + e$^-$ + H$^+$ → H$_2$O

Combining sets of equations (a, b, c) with (A, B, C, D), Stumm and Morgan (1996) show that the free energy changes which occur during the oxidation of Fe(II) by oxygen are more negative for the oxidation of Fe(OH)$^{2+}_{2(aq)}$ than for either Fe(OH)$^+$ and Fe$^{2+}$. In all three reactions a, b, c step A is endergonic but is least endergonic for reaction b; and for all three reactions a, b, c steps B, C, D are all exergonic but in each case reaction b is the most exergonic.

Thus, by explicitly making a kinetic argument from thermodynamic data, Stumm and Morgan (1996) deduced that step A is the slowest step in each case (because it is the most endergonic) and is therefore rate-limiting; and that step A is the fastest for reaction b (because, of the three, it is the least endergonic). Similarly, they deduce that since reaction b is most exergonic for steps B, C, D, all in all Fe(OH)$^0_{2(aq)}$ produces the fastest oxidation sequence. This conclusion is backed up by two other sources. Firstly, it has been shown that ‘hydrolysed’ ferrous iron species are more readily oxidized than non-hydrolysed ferrous species in the following order Fe(OH)$^0_{2(aq)}$ → Fe(OH)$^+$ → Fe$^{2+}$, the reason presumably being that OH$^-$ ligands donate electron density through both the $\sigma$ and $\pi$ systems to the reduced metal ion which increases reducing power and stabilizes the Fe$^{2+}$ formed during the oxidation (Luther, 1990). This hypothesis was experimentally substantiated (in retrospect) by Millero (1985), who showed that the rate constant for the oxidation of Fe(OH)$^0_{2(aq)}$ is five orders of magnitude higher than the rate constant for FeOH$^+$, which, in turn, is five orders of magnitude greater than the rate constant for Fe$^{2+}$ reported by Lowson (1982). Secondly, Wehrli (1990) showed a linear free energy relationship between
the free energy of the reaction (log $K$) and the rate (log $k$) of the reaction for the oxidation of Fe$^{2+}$, FeOH$^+$ and Fe(OH)$_2^{2+}$. Based on the studies of Lowson (1982) and Miller (1985) the following explicit rate equation for soluble ferrous species oxidation can be written. Note that no rate constant has been reported for the oxidation of Fe(OH)$_2^{2+}$ probably due to empirical limitations, however the concentration of this species is exceptionally low at pH values $<\sim$ pH 10 and thus from a practical standpoint this rate constant is of a lesser importance. Also note that the rate constants in Eq. (7) should probably be considered only with respect to their order of magnitude, rather than as accurate quantities.

$$\frac{-d[Fe^{2+}]}{dt} = \left( \frac{6 \times 10^{-5} \cdot Fe^{2+}}{1 + K_{Fe^{2+}} + K_{Fe^{2+}K^{+}} + K_{Fe^{2+}K^{2+}}} \right) + \left( \frac{1.7 \cdot Fe^{2+}}{1 + K_{Fe^{2+}K^{+}} + K_{Fe^{2+}K^{2+}}} \right) + \left( \frac{4.3 \times 10^{-5} \cdot Fe^{2+}}{1 + K_{Fe^{2+}} + K_{Fe^{2+}K^{+}} + K_{Fe^{2+}K^{2+}}} \right)$$  (7)

where $-d[Fe^{2+}]/dt$ is the rate of ferrous oxidation in mole Fe(II) per litre per min. Rate constants were determined with $p_{O_2} = 0.2$ bar.

The effect of ionic strength and temperature on Eq. (7) is determined correspondingly by adjusting the equilibrium constants by the Davis equation (based on the Debye–Huckel approach) and the Van’t Hoff equation (Benjamin, 2002).

Having established the relative rates of oxidation of Fe(II) species one can now rationally explain the oxidation rate curve seen in Figs. 1 and 2. It has already been established that Fig. 3 applies only to Fe(II) solutions at pH $<\sim$8. Examination of Fig. 3 shows that in this pH range the concentrations of FeOH$^+$ and Fe(OH)$_2^{2+}$ rise steeply and linearly with pH. Since these species (especially Fe(OH)$_2^{2+}$) are far more readily oxidized than Fe$^{2+}$ is, this explains the pH-dependence of the oxidation rate between pH $\sim$4–8. Indeed, above pH $<\sim$5 both the first two terms on the right hand side of Eq. (2) fall away (Stumm and Morgan, 1996), which accounts for the second order dependence of the rate law shown in Eq. (1) for this pH region. Below pH $\sim$4 the concentrations of FeOH$^+$ and Fe(OH)$_2^{2+}$ are so low as to be negligible and Fe$^{2+}$ dominates. Since the oxidation of Fe$^{2+}$ is independent of hydroxyl groups, the oxidation rate is no longer pH dependent.

As already established for all pH values above $\sim$8, all Fe(II) solutions of the order of at least $10^{-3}$ molar concentration (again, under the assumption that ferrous complexes only with H$_2$O; in the presence of other complexing or ion pairing agents saturation pH increases, and in the presence of the carbonate system FeCO$_3^{2-}$ rather than Fe(OH)$_2^{2+}$ dominates) will be saturated solutions. Fig. 4 shows the speciation of Fe(II) in two phase aqueous-solid equilibrium. Here at pH $\sim$8 although Fe$^{2+}$ exceeds both FeOH$^+$ and Fe(OH)$_2^{2+}$ in concentration, the latter two species are far more easily oxidized due to the presence of the hydroxyl groups. As one moves from pH $\sim$8 to the right in Fig. 4, both the Fe$^{2+}$ and FeOH$^+$ concentrations drop steeply whilst the Fe(OH)$_2^{2+}$ concentration is constant. As the pH increases above 8.0 the oxidation rate (Eq. (2)) therefore becomes dominated by FeOH$^+$. Since this species is constant with respect to pH ‘throughout’ the range, the rate above pH $\sim$8 becomes independent of pH.

Note that although Fig. 4 shows the Fe(OH)$_2^{2+}$ concentration is constant below pH $\sim$8, in practice this never arises for the reasons stated above, i.e. all Fe(II) solutions of concentrations of the order of $10^{-3}$ M are unsaturated below pH $\sim$8 and single phase liquid equilibrium (Fig. 3) rather than two phase aqueous-solid equilibrium (Fig. 4) applies. As the pH moves below $\sim$8 the threshold for saturation rises logarithmically so that in practise saturated Fe(II) solutions hardly ever occur at pH $<\sim$8.

2. A simple heuristic description

The arguments above account for the shape of the curve describing the oxidation rate of Fe(II) in solution versus pH plot. Taken together, the approach suggests a sigmoid-shaped curve for the Fe(II) oxidation rate as a function of pH as seen in Figs. 1 and 2. This is because:

- At pH values below $\sim$4, Fe$^{2+}$ dominates in Eq. (2) (see Fig. 3).
- At pH $>\sim$5, Fe(OH)$_2^{2+}$ dominates in Eq. (2) because it is far more readily oxidized than Fe$^{2+}$ and FeOH$^+$ as reflected by the magnitude of its rate constant.
- Between pH 5 and 8 the Fe(OH)$_2^{2+}$ concentration rises strongly with pH (Fig. 3), and the oxidation rate increases accordingly.
- At pH values $>\sim$8 Fe(OH)$_2^{2+}$ dominates in Eq. (2) and its concentration does not vary with pH.

In saturated Fe(II) solutions Eq. (2) reduces to $\frac{-d[Fe^{2+}]}{dt} = kDO$ because the [Fe(OH)$_2^{2+}$] concentration is constant (or in Eq. (1) the solubility product is a constant). Thus, at pH $<\sim$7–8 the rate limiting factor governing the oxidation rate appears to be pH whereas at higher pH values, the DO concentration is the rate-limiting factor.

Fig. 5 shows the change in concentration with time of ferrous in aqueous solution as a consequence of oxidation by oxygen at different (constant) pH values. Although the exact positive of the curves depend upon temperature and a variety of other factors (see remarks below), Fig. 5 provides an extremely simple heuristic model reflecting the dramatic differences in oxidation kinetics of ferrous in aqueous solution which occur as a function of pH.

The presented approach can be complemented by the following observations:
3. Conclusions

- It has been observed that catalysts such as Co$^{2+}$ and Cu$^{2+}$ dramatically enhance the oxidation rate (Stumm and Lee, 1961).
- The presence of anions such as Cl$^-$, CO$_3^{2-}$ and SO$_4^{2-}$ have been shown to retard the oxidation rate (Millero, 1985) because they form complexes with Fe(II) that are less favourably oxidized as compared to the hydroxide complexes. The exact rate constants associated with each of these complexes have not been established to date. Part of the difference in the rate curves for seawater and water seen in Fig. 2 are a consequence of such anion effects, the other part being due to temperature.
- In water high in alkalinity (such as ground waters) the overall solubility of Fe(II) is lower and controlled by siderite rather than by ferrous hydroxide. However, the principles governing the rate equation (Eq. (7)) remain valid.

3. Conclusions

- The fundamental equilibrium and thermodynamic principles governing the pH dependent (~5 < pH < ~8) and pH independent (~5 > pH > ~8) kinetics of oxidation of ferrous iron to ferric iron where oxygen is the oxidizing agent have been described. The result is a simple heuristic description of the oxidation kinetics as a function of pH. The visual simplicity of this model assures that it can be easily remembered and applied to any situation where it may be needed.
- The oxidation rate is both thermodynamically and kinetically enhanced by adsorption of dissolved iron species to hydrous oxide surfaces. This is also because of the association with OH$^-$ (Stumm and Morgan, 1970).
- The rate constants of the three meaningful Fe(II) soluble species (Fe$^{2+}$, FeOH$^+$, Fe(OH)$_2^+$) differ from each other by five orders of magnitude ($6 \times 10^{-5}$, 1.7, and $4.3 \times 10^5$ 1/min), respectively. In practical terms this means that the overall oxidation rate depends dramatically on the distribution of these three species in the aqueous phase, which is mostly pH dependent, but to a lesser degree also depends on temperature and ionic strength.
- No rate constant has been reported for the oxidation of Fe(OH)$_2$ probably due to empirical limitations, however the concentration of this species is exceptionally low at pH values < ~pH 10 and thus from a practical standpoint its rate constant is of a lesser importance.
- Further empirical work is required in order to quantify the rate constants of common complexes of Fe(II), encountered in natural waters. Such study is imperative for design purposes of, for example, oxidation reactors aimed at treatment of acid mine drainage, comprising a variable, but always high SO$_4^{2-}$ concentration, or for Fe(II) containing groundwater that also includes a high Cl$^-$ concentration.

References