

Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions

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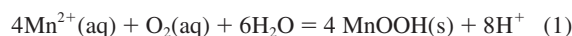
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Abstract—The objective of this research is to assess critically the experimental rate data for O₂ oxidation of dissolved Mn(II) species at 25°C and to interpret the rates in terms of the solution species of Mn(II) in natural waters. A species kinetic rate expression for parallel paths expresses the total rate of Mn(II) oxidation as $\sum k_i a_{ij}$, where k_i is the rate constant of species i and a_{ij} is the species concentration fraction in solution j . Among the species considered in the rate expression are Mn(II) hydrolysis products, carbonate complexes, ammonia complexes, and halide and sulfate complexes, in addition to the free aqueous ion. Experiments in three different laboratory buffers and in seawater yield an apparent rate constant for Mn(II) disappearance, $k_{app,j}$ ranging from 8.6×10^{-5} to 2.5×10^{-2} (M⁻¹ s⁻¹), between pH 8.03 and 9.30, respectively. Observed values of k_{app} exceed predictions based on Marcus outer-sphere electron transfer theory by more than four orders of magnitude, lending strong support to the proposal that Mn(II) + O₂ electron transfer follows an inner-sphere path. A multiple linear regression analysis fit of the observed rates to the species kinetic rate expression yields the following oxidation rate constants (M⁻¹ s⁻¹) for the most reactive species: MnOH⁺, 1.66×10^{-2} ; Mn(OH)₂, 2.09×10^1 ; and Mn(CO₃)₂²⁻, 8.13×10^{-2} . The species kinetic rate expression accounts for the influence of pH and carbonate on oxidation rates of Mn(II), through complex formation and acid-base equilibria of both reactive and unreactive species. At pH ~8, the greater fraction of the total rate is carried by MnOH⁺. At pH greater than ~8.4, the species Mn(OH)₂ and Mn(CO₃)₂²⁻ make the greater contributions to the total rate. Copyright © 2005 Elsevier Ltd

1. INTRODUCTION

Oxidation of manganese (II), to the higher oxidation states Mn(III) and Mn(IV) by dissolved oxygen, is one of the principal processes regulating the rate of manganese cycling in aqueous geochemistry. For example, the overall reaction



transforms the dissolved Mn(II) species into a sparingly soluble Mn(III) oxyhydroxide phase. The product is subject to removal to the sediments of a water body and/or further oxidation to an MnO₂(s) phase in the water column. Mn(III) and Mn(IV) solid phases are subject to reduction by organic carbon compounds and other reductants with a return to the Mn(II) state. Vertical and horizontal profiles of dissolved manganese (largely Mn(II) species) in fresh and marine water bodies thus are established by the dynamics of these oxidation and reduction processes (Johnson et al., 1996).

1.1. Pathways of Mn(II) Oxidation

How rapid is oxidation of manganese by oxygen? An answer depends upon those pathways available in a particular water environment, e.g., biologic, oxide surface catalysis, or homogeneous solution oxidations.

1.1.1. Bacterial oxidation

Mn(II) is oxidized by a wide variety of bacteria. Multicopper enzymes are thought to be essential components of Mn(II)

oxidation in bacteria. Mechanisms and functions of bacterial Mn(II) oxidizing systems have been reviewed by Brouwers et al. (2000). Enzymatic Mn(II) oxidation by *Bacillus* spores has been analyzed by Francis and Tebo (2002). Experiments with waters of marine environments, where Mn(II) concentrations are high and dissolved O₂ levels low, reveal rapid oxidation of Mn(II) by bacteria when compared to rate estimates of abiotic processes (Tebo, 1991; Moffett and Ho, 1996). Kinetics of bacterial Mn(II) oxidation in a variety of natural waters (e.g., near deep ocean vents and in the Black Sea) have been described by a “Michaelis-Menten”-like saturation expression:

$$V = V_{\max}[\text{Mn(II)}]/(K_S + [\text{Mn(II)}]).$$

Reported $V_{\max}$ values range from 5×10^{-4} to 70 nM hr⁻¹; K_S ranged from 10^{-3} to 5 μM (Morgan, 2000). For [Mn(II)] small with respect to K_S , $V \approx (V_{\max}/K_S)[\text{Mn(II)}]$, and the first-order rate constant for bacterial Mn(II) oxidation ranges from ~10 to 10⁻¹ hr⁻¹. The parameters $V_{\max}$ and K_S are, of course, characteristics of the responsible bacterial species and their biomass concentrations.

Kinetics of Mn(II) oxidation by the bacterium *Leptothrix discophora* SS1 have been investigated under controlled laboratory conditions (Zhang et al., 2002). The rate law reported is: $-d[\text{Mn(II)}]/dt = k[X][\text{Mn(II)}]/(K_S + [\text{Mn(II)}])$, where k is an oxidation velocity per biomass, $[X]$ is biomass concentration, and K_S a Michaelis-Menten half-saturation constant. From the detailed results of Zhang et al. (2002) we may calculate a rate constant in natural waters with bacterial Mn(II) oxidizers similar to *Leptothrix*.

For pH 8, $P_{\text{O}_2} \approx 0.21$ atm, 25°C, $[X]$ of 1 mg/L, and [Mn(II)] < K_S , we obtain a first order rate constant for oxidation of 4×10^{-2} hr⁻¹ (compare with 10⁻¹ hr⁻¹ for marine waters, above).

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1.1.2. Metal oxide catalysis

Metal oxide surfaces are able to accelerate Mn(II) oxidation by O_2 . Examples are provided by hematite and manganese dioxide (Wilson, 1980), lepidocrocite (Sung and Morgan, 1981), and goethite and lepidocrocite (Davies and Morgan, 1989). The rate expression proposed by Davies and Morgan (1989) takes the form:

$-d[Mn(II)]/dt \approx k''\beta_2^s \{SOH\} [Mn^{2+}] [H^+]^{-2} A P_{O_2}$ if $[Mn(II)]$ is small in comparison to $A\{SOH\}$. The surface oxidation rate constant, k'' , for lepidocrocite (25°C) is $0.05 \text{ min}^{-1} \text{ atm}^{-1}$. The surface complexation constant β_2^s is $3 \times 10^{-13} \text{ mol l}^{-1}$. The surface site density, $\{SOH\}$, is 0.002 mol g^{-1} . For pH 8, $P_{O_2} = 0.21 \text{ atm}$, and $A = 1 \text{ mg/L}$ of oxide particles, we obtain a first order rate constant for Mn(II) oxidation, 10^{-3} hr^{-1} .

1.1.3. Homogeneous solutions

It was proposed by Diem and Stumm (1984) that Mn^{2+} is not oxidized by O_2 in the absence of bacteria or surface catalysts. Careful examination of the data in their paper suggests that oxidative removal of Mn(II) with O_2 did occur in initially homogeneous solutions at ca. pH 8. The half-life for Mn(II) disappearance may be estimated to be in the range 200 to 300 days (20°C, air saturation, $7.5 \text{ }\mu\text{M}$ initial Mn(II) concentration). The pseudo first-order rate constant for oxidation would be on the order of 10^{-4} hr^{-1} . Von Langen et al. (1997) report a pseudo first-order rate constant of $6.7 \times 10^{-5} \text{ hr}^{-1}$ in seawater at pH 8.16.

1.1.4. Comparisons

On the basis of the limited observations available, we suggest a preliminary comparison of the half-lives for bacterial oxidation, oxide surface catalyzed oxidation, and homogeneous solution oxidation of Mn(II) at pH 8. Bacterial oxidation: 10 hr; oxide catalyzed oxidation: 30 days; homogenous solution oxidation: 400 days.

1.2. Kinetic Analysis of Homogeneous Oxidation

The kinetics of manganese oxidation by O_2 in homogeneous solution need to be understood in a more fundamental and quantitative way. A kinetic analysis requires information on several levels: reaction stoichiometry, energetics, the experimental rate law, a proposed scheme of elementary reactions, and a rate expression based on the proposed scheme. At the molecular level, information on an intimate mechanism can be used to predict the rates of elementary reactions, e.g., that for electron transfer.

1.2.1. Mn(II) oxidation

In brief outline, the stoichiometry of Mn(II) oxidation by dissolved O_2 at moderately alkaline pH is $4 \text{ Mn(II) (aq)} + O_2 = 4 \text{ MnOOH(s)}$. . . Energetic information reveals that there is a substantial free energy barrier to a first one-electron oxidation step, e.g., $Mn^{2+} + O_2 \rightarrow Mn^{3+} + O_2^-$. The experimental rate law for Mn(II) disappearance via oxidation in an initially homogeneous solution has been found to be $-d[Mn(II)]/dt$

$= k_{app} [O_2] [Mn(II)]$, in which k_{app} is a function of temperature, pH, complexing ligands, and ionic strength. A plausible scheme of elementary reactions for Mn(II) oxidation is based on the Haber-Weiss mechanism (Rosso and Morgan, 2002) and is analogous to the parallel path scheme to describe Fe(II) oxidation (Wehrli, 1990; King, 1998). A proposed rate expression can then be formulated on the assumption that all Mn(II) reactant species are at equilibrium throughout the reaction. It is further assumed that the rate-determining step in the overall mechanism is the first one-electron transfer for each Mn(II) species, $Mn(II)_i$, e.g., $Mn(II)_i + O_2 \rightarrow Mn(III)_i + O_2^-$.

Properties of the aqueous species Mn^{3+} , $MnOH^{2+}$, and $Mn(OH)_2^+$ have been reported previously, e.g., by Diebler and Sutin (1964), Biedermann and Palombari (1978), Macartney and Sutin (1985), and Fronaeus et al. (1998). A proposed rate expression on the basis of the foregoing is then $-d[Mn(II)]/dt = 4[O_2] \sum k_i [Mn(II)_i]$. The species rate constant, k_i , depends on the character of the intimate molecular mechanism for the electron transfer step. If the electron transfer occurs by an *outer-sphere* path, i.e., through the intact hydration spheres of O_2 and Mn(II) species, Marcus theory affords a prediction of the species rate constant. If there is bond formation between the O_2 and the Mn^{2+} center, the path is an *inner-sphere* one. No prediction of an inner-sphere species rate constant is presently available. On the grounds of frontier molecular orbital theory, Luther (1990) has argued that an inner-sphere path is more likely for $Mn(II) + O_2$. In the present work, comparison of Marcus theory outer-sphere predictions with the experimental results can shed light on the prevailing mechanism.

1.2.2. Outer-sphere electron transfer

The Marcus theory provides prediction of the electron transfer rate constant for aqueous reactions in which the hydration spheres of reactants remain intact throughout. A rate constant for the overall reaction is described by

$$k = \kappa Z \exp(\Delta G^*/RT) \quad (2)$$

(Marcus, 1997; Marcus and Sutin, 1985), where κ is the electronic transmission coefficient ($\kappa \approx 1$ for adiabatic transfer and $\kappa < 1$ for nonadiabatic transfer, Z is a bimolecular collision frequency, and ΔG^* is the activation free energy of electron transfer.) For example, reaction between $O_2(aq)$ and $Mn(OH)_2(aq)$ yielding O_2^- and $Mn(OH)_2^+$ products entails three steps: (1) bringing the reactants together to form a precursor species to electron transfer, $O_2 - Mn(OH)_2$, in which the reactants are at a close separation distance dictated by their sizes and hydration sheaths; (2) following the required reorganization of nuclear coordinates in the inner- and outer-sphere of each reactant in the complex, an electron is transferred from $Mn(OH)_2$ to O_2 ; and (3) products O_2^- and $Mn(OH)_2^+$ are separated to bulk solution. The great achievement of the Marcus theory is to enable prediction of the activation free energy, ΔG^* , for outer-sphere electron transfer, and hence the electron transfer rate constant, k^{et} . The rate constant for the overall reaction may then be calculated as $k = K^{pre} k^{et}$, where K^{pre} is the equilibrium constant for forming the precursor species (Rosso and Rustad, 2000).

Rosso and Morgan (2002) provided predictions of reaction rates for a number of bivalent transition metal solution species

with O_2 by combining molecular orbital computations and Marcus theory. They computed the energies of steps (1) and (3) above, and the reorganization energies of step (2) to predict k^{et} , K^{pre} , and the observable rate constant $k = K^{pre} k^{et}$ for oxidation of fifteen metal(II) species by O_2 . Details of principles, parameters, and methods of these computations for V, Cr, Mn, Fe, and Co are given in [Rosso and Morgan \(2002\)](#).

For outer-sphere reaction between dissolved O_2 and each of the species Mn^{2+} , $MnOH^+$, and $Mn(OH)_2$, [Rosso and Morgan \(2002\)](#) predicted rate constants $k_{Mn} = 1.6 \times 10^{-18}$, $k_{MnOH} = 6.3 \times 10^{-10}$, and $k_{Mn(OH)_2} = 7.9 \times 10^{-4} (M^{-1}s^{-1})$.

1.3. Objective

The objective of the work reported here is to identify the experimental rate law for O_2 oxidation of dissolved Mn(II) species to Mn(III) product, and to interpret this rate law in terms of the solution species of Mn(II) expected in natural waters. Among these species are aqueous ("free") Mn^{2+} and its hydrolysis products, carbonate complexes, and complexes with other ligands such as sulfate and chloride ([Turner et al., 1981](#)). Groundwork for this kinetic approach has been laid by the work on $Fe(II) + O_2$ kinetics of [Millero \(1985\)](#), [Wehrli \(1990\)](#), and [King \(1998\)](#). Generally, we may anticipate two broad groupings of Mn(II) species in water: those which are slowly reacting or essentially nonreactive with O_2 , and those which react at appreciable rates.

The rate of Mn(II) disappearance from solution caused by O_2 oxidation is represented by a rate expression that is a sum of individual rates for different species along parallel reaction paths. For instance

$$-d[Mn(II)]/dt \equiv R = R_{Mn} + R_{MnOH} + R_{Mn(OH)_2} + R_{MnCO_3} + \dots + R_i = \sum R_i \quad (3)$$

where R_i denotes rate of disappearance of the i th species of Mn(II) in solution. The presence of *nonreactive* species of Mn(II) in water affects Mn(II) oxidation rates by depleting concentrations of reactive species, as shown by [King \(1998\)](#) for the case of $Fe(II)$ oxidation by O_2 .

2. EXPERIMENTAL OBSERVATIONS

2.1. Products of Manganese (II) Reaction with O_2

In fresh and marine waters, typical dissolved manganese (II) concentrations are rarely high enough (nanomolar and micromolar levels, respectively) to exceed solubility limits of $Mn(OH)_2$ solid within the usual ranges of pH. However, early laboratory studies of Mn(II) oxidation rates often were carried out under solution conditions leading to incipient precipitation of an $Mn(OH)_2$ phase ([Nichols and Walton, 1942](#)). Oxidation of $Mn(OH)_2(s)$ by $O_2(aq)$ is very rapid and leads to initial formation of an $Mn_3O_4(s)$ phase ([Morgan, 1964; Bricker, 1965](#)). At lower Mn(II) solution concentrations and lower pH, an Mn(III) solid oxidation product has been observed.

[Kessick and Morgan \(1975\)](#) found that in O_2 -saturated ammonia-ammonium buffer solutions of pH ranging from 8.69 to 8.98, with an initial Mn(II) solution concentration of 0.50 mM (undersaturated with respect to $Mn(OH)_2(s)$ precipitation), the oxidation product, after complete depletion of all Mn(II) from solution, had the composition of an $MnOOH(s)$ phase with an empiric oxidation state formula $MnO_{1.51}$ to $MnO_{1.54}$.

[Stumm and Giovanoli \(1976\)](#) followed the oxidation of 10 μM Mn(II) solutions open to air in the presence of either 2 mM $NaHCO_3$ solutions or 1 mM ammonium nitrate solutions (pH range ca. 8–9).

Visible precipitate formed after ca. 100 to 300 days. The product phase identified in all of their experiments was γ - $MnOOH(s)$ (identified by Mo X-ray diffraction) in the form of long, thin needles. All of the experimental solutions were reported to be undersaturated with respect to $Mn(OH)_2(s)$ precipitation.

2.2. Rate Laws Reported for Mn(II) + O_2 Reactions

Oxidation of Mn(II) in bicarbonate-carbonate solutions was studied by [Hem \(1963\)](#) and [Morgan and Stumm \(1963\)](#). A rate law for autocatalytic oxidation of Mn(II) was proposed by [Morgan \(1964\)](#):

$$-d[Mn(II)]/dt = k_1[Mn(II)] + k_2[MnO_x][Mn(II)] \quad (4)$$

in which $[Mn(II)]$ and $[MnO_x]$ represent concentrations of dissolved reactant and solid oxidized reaction product, respectively, and k_1 is a pseudo first-order rate constant for Mn(II) disappearance from solution. (The solid reaction product was subsequently identified as an Mn (III) oxyhydroxide solid ([Kessick and Morgan, 1975](#)). The pseudo first-order rate constant, k_1 , depended on temperature, oxygen concentration, pH, and Mn(II) species in solution. Higher concentrations of $[HCO_3^-] + [CO_3^{2-}]$ were observed to lower the rate of Mn(II) oxidation.

2.3. Resolved Rates of Homogeneous and Heterogeneous Oxidation

[Sung and Morgan \(1980\)](#) found that reaction between $Fe(II)$ species and O_2 could also proceed heterogeneously and autocatalytically under a limited range of pH and $[Fe(II)]_{total}$ conditions. Integration of a rate law of the form of Eqn. 4 allowed extraction of rate constants k_1 and k_2 for homogeneous and heterogeneous catalytic paths, respectively. Application to the previous kinetic observations of [Morgan \(1964, 1967\)](#) for $Mn(II) + O_2$ yielded resolved sets of values for the homogeneous and heterogeneous rate constants, k_1 and k_2 of Eqn. 4 from experimental results in bicarbonate and ammonium buffer solutions with pH in the range 9.0 to 9.3.

2.4. Homogeneous Oxidation of Mn(II) in Carbonic Buffers at Lower pH

[Davies and Morgan \(1989\)](#) reported experiments on $Mn(II) + O_2$ under conditions of unit oxygen partial pressure, lower $Mn(II)_{total}$ (50 μM), and lower pH in $CO_2 - HCO_3^- - CO_3^{2-}$ solutions. Reaction samples were filtered through 0.22-micron membrane filters before analysis for Mn(II). [Davies \(1984\)](#) demonstrated experimentally that his solutions, while supersaturated with respect to $MnCO_3(s)$, did not yield any precipitate in the absence of dissolved O_2 . Davies' experiments thus yielded homogeneous first order oxidation rate constants, k_1 , in the expression

$$-d[Mn(II)]/dt = k_1[Mn(II)] \quad (5)$$

over the pH range 8.95 to 9.25.

2.5. Homogeneous Oxidation of Mn(II) in Seawater

Oxidation of Mn(II) in filtered coastal Pacific Ocean waters was examined by [Von Langen et al. \(1997\)](#). The concentration of Mn(II) added was 20 nM, and the range of adjusted seawater pH (with NH_3) was from 8.03 to 8.67. Mn(II) concentrations were analyzed directly in seawater by a highly sensitive flow injection analysis with chemiluminescence. They obtained first order rate constants for *homogeneous* oxidation in seawater. The dependence on pH of these observed rate constants (combined with earlier results of [Morgan \(1964\)](#), [Sung and Morgan \(1980\)](#), and [Davies and Morgan \(1989\)](#)) were summarized by [Von Langen et al. \(1997\)](#) in an expression of the form $k_1 = \text{constant} \times [OH^-]^{2.0 \pm 0.3}$.

2.6. Experimental Data Base for Evaluating a Species Kinetics Model

[Table 1](#) summarizes the available pseudo first-order homogeneous solution rate constants, k_1 , for the $Mn(II) + O_2$ reaction at 25°C. The

Table 1. Parameters and observed rate constants for experimental solutions, 25°C.

pH ^a	I ^b /M	P _{O₂} /atm	K _H ^c /M atm	k _{j,1} ^d /s ⁻¹	k _{j,app} /M ⁻¹ s ^{-1e}
<i>1.0 × 10⁻² M ammonium-ammonia buffers^f</i>					
9.30	0.005	1	1.26 × 10 ⁻³	(3.17 ± 0.48) × 10 ⁻⁵	(2.52 ± 0.38) × 10 ⁻²
9.20				(1.53 ± 0.23) × 10 ⁻⁵	(1.22 ± 0.19) × 10 ⁻²
9.00				(3.33 ± 0.50) × 10 ⁻⁶	(2.65 ± 0.40) × 10 ⁻³
<i>3.63 × 10⁻³ M bicarbonate-carbonate buffers^f</i>					
9.00		1	1.26 × 10 ⁻³	(6.00 ± 0.90) × 10 ⁻⁶	(4.77 ± 0.72) × 10 ⁻³
<i>P_{CO2} = 1.42 × 10⁻⁴ atm – NaOH buffers^g</i>					
9.25	0.100	1	1.22 × 10 ⁻³	(9.50 ± 0.67) × 10 ⁻⁶	(7.78 ± 0.55) × 10 ⁻³
9.04				(2.83 ± 0.67) × 10 ⁻⁶	(2.32 ± 0.55) × 10 ⁻³
8.95				(1.50 ± 0.33) × 10 ⁻⁶	(1.23 ± 0.27) × 10 ⁻³
<i>Filtered coastal seawater, salinity = 33^h</i>					
8.67	0.65	0.22	9.68 × 10 ⁻⁴	(1.03 ± 0.32) × 10 ⁻⁷	(4.85 ± 1.49) × 10 ⁻⁴
8.62				(7.00 ± 0.30) × 10 ⁻⁸	(3.28 ± 1.41) × 10 ⁻⁴
8.62				(1.17 ± 0.28) × 10 ⁻⁸	(5.48 ± 1.33) × 10 ⁻⁴
8.46				(6.00 ± 1.15) × 10 ⁻⁸	(2.82 ± 0.54) × 10 ⁻⁴
8.40				(3.17 ± 1.15) × 10 ⁻⁸	(1.49 ± 0.54) × 10 ⁻⁴
8.20				(3.17 ± 0.48) × 10 ⁻⁸	(1.49 ± 0.23) × 10 ⁻⁴
8.16				(1.83 ± 0.70) × 10 ⁻⁸	(8.63 ± 3.28) × 10 ⁻⁵
8.03				(2.33 ± 5.83) × 10 ⁻⁸	(1.10 ± 2.73) × 10 ⁻⁴

^a N.B.S. pH scale.^b Ionic strength.^c Henry's law constant for O₂.^d First-order rate constant for Mn(II) loss.^e k_{app} = k₁/K_H P_{O₂}.^f Original data of Morgan (1964, 1967) reinterpreted by the method of Sung and Morgan (1980).^g Davies and Morgan (1989).^h Von Langen, et al (1997).

rate constant k₁ describes the disappearance of Mn(II). The pH range covered by the data are 8.03 to 9.30. (Observed rates at a few higher pH values (Morgan 1964, 1967) for ammonia and carbonate buffers could not be interpreted because incipient precipitation of Mn(OH)₂(s) or MnCO₃(s) occurred in some of the solutions.)

When the observed first-order rate constants for the various media are normalized to the usual O₂ atmospheric partial pressure (~0.21 atm), the range of Mn(II) half-life with respect to disappearance by homogeneous oxidation is from ca. 340 days to 1 d. Mn(II) reaction with O₂ is indeed slow in comparison with that for Fe(II) (Wehrli, 1990; King, 1998). For example, at pH ≈ 8 in seawater with P_{O₂} ≈ 0.21 atm, approximate half-lives for Mn(II) and Fe(II) disappearance are 340 days and 20 s, respectively.

Table 1 also gives the calculated apparent rate constants, k_{app}, for Mn(II) oxidative disappearance. This apparent rate constant is a pseudo second-order constant, obtained by normalization of different results to unit molar O₂ concentration:

$$k_{app} = k_1/[O_2] = k_1/K_H P_{O_2} \quad (6)$$

where K_H is the applicable Henry's law constant for O₂ (M atm⁻¹) in a solution of known salt concentration, and P_{O₂} is oxygen partial pressure (atm). As explained below in describing the species kinetic model (Section 3), it is necessary to introduce the quantity (k_{app}/4) to compare experimental results and a rate expression prediction of oxidation rates.

Figure 1 presents a plot of log (k_{app}/4) vs. pH for the experimental results used to fit the species rate constants in the proposed rate expression. Results from laboratory buffer solutions and seawater are included. The observed rate constants span almost three orders of magnitude in the pH range 8.03 to 9.30.

Because concentrations of Mn(II) complexing ligands in seawater,

carbonate buffers, and ammonia buffers differ significantly from one another in their pH dependence, the results in Figure 1 are not amenable to a simple chemical interpretation. The general trend of rate constants with pH may reflect several proton-dependent speciation reactions. The seawater data (because of Mn(II) complexes with sulfate and chloride ions as well as hydroxide, carbonate, and bicarbonate ions) may stand apart from the data obtained in different laboratory buffers (as these data are expected to differ from each other). For example, absence of carbonate species limits Mn(II) speciation to hydroxo and NH₃ complexes. A fixed P_{CO₂} system buffer usually differs from a closed (C_T) buffer in free carbonate ion concentration and in pH dependence of complexation.

Following examples of kinetic studies on different Fe (II) species as reductants for various oxidants reported by Buerge and Hug (1997), King (1998), and Strathmann and Stone (2002), the contributions of a number of aqueous Mn(II) species to reduction of O₂ need to be evaluated. In doing so we consider the equilibrium speciation of Mn(II) in media of different pH, ligand concentrations, and ionic strengths.

3. A KINETIC RATE EXPRESSION FOR Mn(II) + O₂

3.1. Framework

Experimental observations of Mn(II) oxidation reveal that: (1) the rate of Mn(II) disappearance is first order in Mn(II) concentration; (2) the rate is proportional to O₂ concentration; (3) the product of reaction is MnOOH(s) in the pH range ca. 8 to 9.5; and (4) the rate increases dramatically with increasing pH.

It is proposed: (i) that the reactions between Mn²⁺ and all considered ligands in solution are at equilibrium; (ii) that

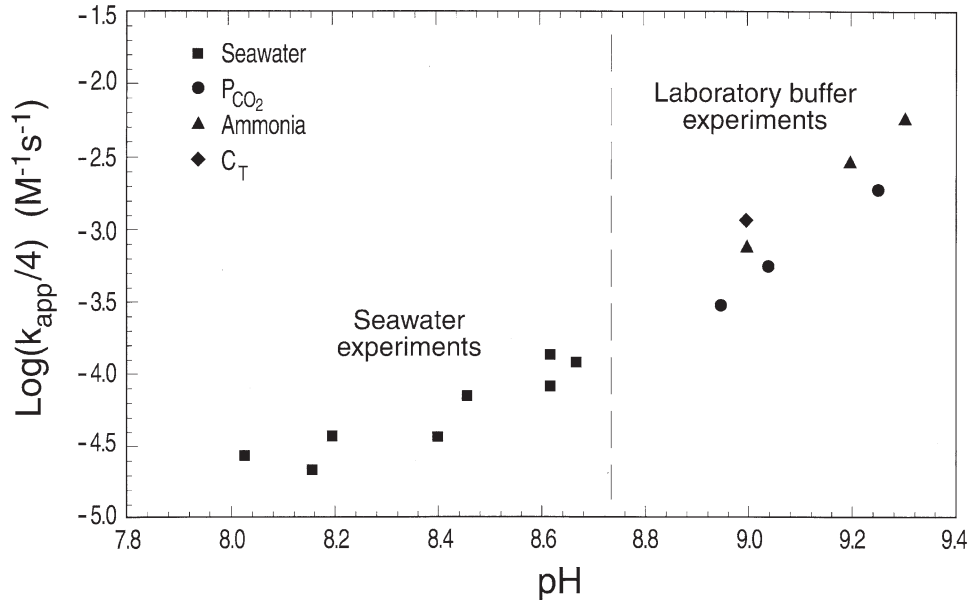


Fig. 1. Experimental rate constant data: $\log k_{j,app}/4$ vs. pH. $k_{j,app}$ is the first-order rate constant at 25°C for Mn(II) disappearance, normalized to unit dissolved O_2 molarity.

reaction of dissolved oxygen with each Mn(II) species proceeds stepwise from O_2 to O_2^- to H_2O_2 , to OH^- , and on to H_2O ; (iii) that the first step for each Mn(II) species in this reaction sequence, e.g., $Mn^{2+} + O_2 \rightarrow Mn^{3+} + O_2^-$, $MnOH^+ + O_2 \rightarrow MnOH^{2+} + O_2^-$, $Mn(OH)_2 + O_2 \rightarrow Mn(OH)_2^+ + O_2^-$, and $Mn(CO_3)_2^{2-} + O_2 \rightarrow Mn(CO_3)_2^- + O_2^-$ is the rate determining step for oxidation of that species (There have been no direct observations of the Mn(III) biscarbonato species. The corresponding Fe(III) species has been reported by Bruno and Duro (2000). The first step in the four-step reduction of O_2 is a slow step in comparison to succeeding reductions of O_2^- , H_2O_2 , and OH^- ; and (iv) intermediate Mn(III) species formed in the oxidations are progressively transformed to $MnOOH(s)$ via hydrolysis, nucleation, and precipitate formation. It follows from the foregoing observations and assumptions that the rate of Mn(II) disappearance is four times the rate of reduction of O_2 , i.e., $-d[Mn(II)]/dt = -4 d[O_2]/dt$.

In a given aqueous system the various equilibrium species concentrations can be computed from a knowledge of the system components, e.g., total carbonate, chloride, sulfate, ammonia, and acids, bases, and salts (fixing the pH and ionic strength), together with equilibrium constants that have been corrected for ionic strength. For example, in a dilute buffer solution comprising NH_4^+ , NH_3 , Mn(II) salt, fixed pH, and $NaClO_4$ background electrolyte, the Mn(II) species of interest include Mn^{2+} , $MnOH^+$, $Mn(OH)_2$, $Mn(OH)_3^-$, $MnNH_3^{2+}$, and $Mn(NH_3)_2^{2+}$ (neglecting species with the weak ligand perchlorate). An appropriate kinetic rate expression is then:

$$-d[Mn(II)]/dt = 4[O_2]\{k_{Mn}[Mn^{2+}] + k_{MnOH}[MnOH^+] + k_{Mn(OH)_2}[Mn(OH)_2] + k_{Mn(OH)_3^-}[Mn(OH)_3^-] + k_{MnNH_3}[MnNH_3^{2+}] + k_{Mn(NH_3)_2}[Mn(NH_3)_2^{2+}]\} \quad (7)$$

in which k_{Mn} , etc., are rate constants for oxidation of species by O_2 .

Defining the fraction of total manganese (II) concentration present in species i in a solution j as a_{ij} , e.g., $a_{Mn,j} = [Mn^{2+}]_j / [Mn(II)]_j$, and so forth, we obtain the rate expression for the disappearance of Mn(II) via oxidation in a particular solution:

$$k = 4 \{k_{Mn} a_{Mn} + k_{MnOH} a_{MnOH} + \dots + k_{Mn(NH_3)_2} a_{Mn(NH_3)_2}\} \quad (8)$$

(Note that a_{Mn} is a concentration fraction in solution, not a thermodynamic activity nor a mole fraction.) For solution j with various species fractions a_{ij} and species rate constants k_i , the computed rate constant for Mn(II) disappearance is

$$k_j = 4 \sum k_i a_{ij} \quad (9)$$

If the species rate constants, k_i , are already available, e.g., from theory, such as the Marcus theory for outer-sphere electron transfer (Rosso and Morgan, 2002), and the species fractions, a_{ij} , can be computed for each solution environment, then Eqn. 9 enables prediction of Mn(II) disappearance rates in solution j for an *outer-sphere* pathway.

Alternatively, values of $k_{j,app}$ from experiments (Table 1), together with a set of rate constant expressions of a similar form as Eqn. 9, for example

$$k_{j,app} \{\text{compare}\} 4 \sum k_{i,fit} a_{ij} \quad (10)$$

offer a framework for best-fit estimates of the species rate constants, $k_{i,fit}$, employing multiple linear regression analysis and the method of least squares. The species fractions a_{ij} are calculated from the solution composition for each experiment employing appropriate equilibrium constants (which have been corrected for ionic strength). The pH and metal and ligand concentrations together determine Mn(II) speciation in experimental solutions.

Table 2. Equilibrium reaction constants for the experimental solutions, 25°C.

Reaction	Log K_{eq} ^a
$H_2O = H^+ + OH^-$	-14.00
$CO_2(aq) + H_2O = HCO_3^- + H^+$	-6.35
$CO_2(g) = CO_2(aq)$	-1.47
$HCO_3^- = CO_3^{2-} + H^+$	-10.33
$O_2(g) = O_2(aq)$	-2.90
$NH_4^+ = NH_3(aq) + H^+$	-9.24
$Mn^{2+} + H_2O = MnOH^+ + H^+$	-10.6 ^b
$Mn^{2+} + 2H_2O = Mn(OH)_2 + 2H^+$	-22.2
$Mn^{2+} + 3H_2O = Mn(OH)_3^- + 3H^+$	-34.8
$Mn^{2+} + 4H_2O = Mn(OH)_4^{2-} + 4H^+$	-48.3
$Mn^{2+} + CO_3^{2-} = MnCO_3(aq)$	4.4 ^c
$Mn^{2+} + 2CO_3^{2-} = Mn(CO_3)_2^{2-}$	5.7
$Mn^{2+} + CO_3^{2-} + H^+ = MnHCO_3^+$	11.6
$Mn^{2+} + CO_3^{2-} + H_2O = MnOHCO_3^- + H^+$	-6.1 ^d
$Mn^{2+} + NH_3 = MnNH_3^{2+}$	1.0 ^e
$Mn^{2+} + 2NH_3 = Mn(NH_3)_2^{2+}$	1.5 ^e
$Mn^{2+} + Cl^- = MnCl^+$	0.66 ^f
$Mn^{2+} + SO_4^{2-} = MnSO_4(aq)$	2.3 ^e
$Mn^{2+} + F^- = MnF^+$	1.3 ^e

^a Acid-base constants and gas solubility constants from Stumm and Morgan (1996).

^b Hydrolysis constants from Baes and Mesmer (1976).

^c $MnCO_3$ and $Mn(CO_3)_2^{2-}$ constants from linear free energy relationship with oxalate complexes (Langmuir, 1979).

^d From extrapolation to 25°C of higher-temperature data of Wolfram and Krupp (1996).

^e Martell and Smith (2003).

^f Turner et al. (1981); see Section 3.2.1. for details.

3.2. Species Concentration Fractions

Equilibrium constants required for reduction of the experimental data from k_1 to k_{app} and those acid-base and Mn(II) complex formation reactions pertinent to the species concentration calculations are collected in Table 2. O_2 and CO_2 solubility values are appreciably different in seawater and in dilute buffer solutions. Salt corrections were necessary to the Henry's constants in the table. The O_2 solubility in seawater was that employed by Von Langen et al. (1997). CO_2 solubility data under different ionic strength conditions are from Stumm and Morgan (1996). Ionic strength corrections for seawater acid base and complex stability are based on the computations of Turner et al. (1981). $[CO_3^{2-}]_{free}$, $[HCO_3^-]_{free}$ and other free ligand concentrations for mass law expressions are those of Turner et al. (1981). Buffer solution equilibrium constants were corrected for ionic strength with the Davies equation (Stumm and Morgan, 1996). The NBS pH scale was used for seawater (Von Langen, et al., 1997) and for laboratory solutions. A salting coefficient for O_2 in 0.1 M $NaClO_4$ solution was estimated from data in Harned and Owen (1958).

3.2.1. Selection of Mn(II) species stability constants

Calculation of Mn(II) species fractions in solution requires careful choice of the equilibrium constants. Our selection process begins with reference to NIST's *Critically Selected Stability Constants of Metal Complexes, Version 7* (Martell and Smith, 2003). For Mn^{2+} the critically selected values of the equilibrium constants for species formed with the ligands OH^- , CO_3^{2-} , NH_3 , Cl^- , SO_4^{2-} , and F^- were examined. If a particular

selection in the NIST compilation appeared questionable, primary data sources were next consulted using the bibliographic information in Martell and Smith (2003). An earlier assessment of hydrolysis species of Mn^{2+} by Baes and Mesmer (1976) was also examined in detail for this work.

The stability constants of the species $MnNH_3^{2+}$, $Mn(NH_3)_2^{2+}$, $MnSO_4$, and MnF^+ adopted here are those in the compilation by Martell and Smith (2003). They are included in Table 2.

Hydroxide complexes. In the case of the hydroxide complexes $MnOH^+$, $Mn(OH)_2$, $Mn(OH)_3^-$, and $Mn(OH)_4^{2-}$, the stability constants adopted here are those first cited by Baes and Mesmer (1976), which were derived from the earlier experiments of Fox et al. (1941) on $Mn(OH)_2(s)$ solubility. These constants are also the critically selected values of Martell and Smith (2003). They are included in Table 2. It should be noted that the stability constants for $MnOH^+$ and $Mn(OH)_4^{2-}$ were experimentally derived quantities, whereas those for the intermediate species were proposed by Baes and Mesmer (1976) on the basis of a "regular progression" of stabilities. (In examining the stabilities of the four corresponding hydroxide species for the bivalent metals Fe(II), Ni(II), Zn(II), and Co(II) (Martell and Smith, 2003), the choices for Mn(II) appear reasonable. We are guided here by the same criteria invoked by Martell and Smith (2003) in pursuing comparison with other metals for the same ligand and with other ligands for Mn(II) when experimental data are limited. For example, the Irving Williams series (Stumm and Morgan, 1996) is a helpful guide in comparison. With no ligand-field stabilization energy in Mn(II) complexes, we are inclined to discount reported high values of some species, e.g., a stability constant of $10^{-18.5}$ for the species $Mn(OH)_2$ reported by Wolfram and Krupp (1996), as compared to the critically selected value of $10^{-22.2}$ in Martell and Smith (2003).

The species Mn_2OH^{3+} and $Mn_2(OH)_3^+$ are also part of the compilation of Martell and Smith (2003). Reference to the work of Baes and Mesmer (1976) traces these two proposed species to experiments of Fontana and Brito (1968), who employed 1.0 M sulfate in all solutions and very high Mn(II) concentrations. Baes and Mesmer (1976) stated, concerning these dimeric species, that "their identity is poorly established because of the high concentrations of Mn(II) at which they occur." Our computations indicate that the stability constants proposed for these dimers would yield total manganese solution concentrations in 15-fold excess of measured $Mn(OH)_2(s)$ solubility in the pH range 8 to 9. For these reasons the dimeric species are not included here.

Carbonate complexes. Mn(II) complexes with carbonate are represented by two species in the compilation of Martell and Smith (2003): $MnHCO_3^+$ and $MnCO_3$. The critically selected stability constant for the bicarbonate complex, $10^{1.3}$, is from two independent determinations under dilute solution conditions (Lesht and Baumann, 1978; Emara et al., 1985). Both lower and higher stabilities for $MnHCO_3^+$ are reported in the bibliography: $10^{0.76}$ (Néher-Neumann, 1994) and $10^{2.2}$ (Wolfram and Krupp, 1996). The selection by Martell and Smith (2003), $10^{1.3}$, appears reasonable for an ion pair. It is included in Table 2.

The stability constant selected for the species MnCO_3 in the critical compilation of Martell and Smith (2003) is $10^{4.7}$. This infinite dilution value was obtained by recalculation from experimental results for 3 M NaClO_4 medium (Néher-Neumann, 1994) employing the Specific Ion Interaction Theory model for ion activity coefficients. Using the same model (Grenthe et al., 1997) for recalculation of the 3 M ionic strength measurements of Néher-Neumann (1994) in this work, we obtain $10^{4.5}$ for the MnCO_3 stability (with ion interaction coefficients $\varepsilon(\text{CO}_3^{2-}, \text{Na}^+) = -0.08$ and $\varepsilon(\text{ClO}_4^-, \text{Mn}^{2+}) = 0.38$). From a linear free energy regression (LFER) of bivalent metal stability constants of oxalate ion and carbonate ion we estimate an MnCO_3 stability constant ($I = 0$) is $10^{4.4}$ (Langmuir, 1979). (A higher experimental value of the stability constant, $10^{4.96}$, was obtained by Wolfram and Krupp (1996), and a lower value of $10^{4.1}$ was estimated using an LFER by Grenthe et al. (1997).) We have chosen an MnCO_3 stability constant of $10^{4.4}$ on the basis of our assessment of the primary literature. This value is included in Table 2.

$\text{Mn}(\text{CO}_3)_2^{2-}$ complex. A comparison with Fe(II) and other first row transition elements leads one to expect a biscarbonato species in solution. King (1998) interpreted Fe(II) solubility data to obtain a value of $10^{7.45}$ for the $\text{Fe}(\text{CO}_3)_2^{2-}$ complex. A lower value is anticipated for the corresponding Mn(II) complex on chemical grounds. From an LFER between carbonate and oxalate biscarbonato stability constants (Langmuir, 1979), we obtain the value $10^{5.7}$ for $\text{Mn}(\text{CO}_3)_2^{2-}$. This value is included in Table 2.

MnOHCO_3^- species. Stability constants for this mixed-ligand complex were obtained at temperatures of 90° and 200°C using rhodochrosite mineral solubility measurements (Wolfram and Krupp, 1996). We have extrapolated these results to 25°C, thereby estimating a stability constant of $10^{-6.1}$ for the reaction $\text{Mn}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O} = \text{MnOHCO}_3^- + \text{H}^+$ (compare $10^{-4.0}$ for FeOHCO_3^- of King (1998)). It is recognized that our estimate of this stability constant is somewhat uncertain and may be on the low side. Table 2 includes the value of $10^{-6.1}$ for the species.

MnCl^+ complex. The stability of the chloride complex of Mn(II) is small and uncertain. The seawater model of Turner et al. (1981) employed the infinite dilution stability constant $10^{0.66}$ for MnCl^+ (corrected to a value of $10^{0.06}$ for ionic strength 0.65 M seawater.) A very recent critical estimate of the stability constant on the basis of all credible data places the infinite dilution value closer to $10^{0.0}$ (Martell and Smith, 2003). The experimental work of Carpenter (1983) implies a seawater stability constant of $\sim 10^{-0.46}$, based on electron spin resonance measurements of Mn in seawater and corresponding electrolyte solutions of similar ionic strength. Byrne et al. (1988) proposed an MnCl^+ stability constant in seawater of $10^{-0.28}$, based on their recalculation of earlier data. Our own choice is twofold. Table 2 includes the constant $10^{0.66}$, following Turner et al. (1981). Secondly, we have repeated our seawater species calculations with an MnCl^+ stability constant of $10^{-0.3}$ to evaluate the consequences of a much lower stability.

3.2.2. Species fractions in experimental solutions

The results of Mn(II) species concentration fraction computations for fifteen experiments are presented in Table 3. Several species concentration fractions are plotted vs. pH in Figure 2 (Some of the Mn(II) complexes are omitted in this figure for clarity.) The species fractions for the seawater experiments, in which only pH is varied under assumed closed system conditions, vary smoothly with pH. Linear regressions for $\log a_i$ vs. pH give the following slopes for seawater: MnOH^+ , 0.946; $\text{Mn}(\text{OH})_2$, 1.947; $\text{Mn}(\text{OH})_3^-$, 2.945; and $\text{Mn}(\text{CO}_3)_2^{2-}$, 1.877.

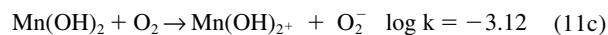
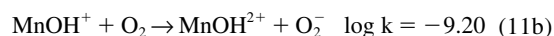
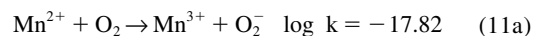
A detailed but readily interpreted pattern of species fractions vs. pH is shown for the laboratory buffers. It can be seen that in the ammonia buffers the fraction of Mn^{2+} is near unity, whereas in seawater it is near 0.5, a consequence of Mn(II) complexation by chloride and sulfate ("MnX"), and to a lesser extent, carbonate. In the P_{CO_2} buffers, the concentration of Mn^{2+} is lower than in the ammonia buffers, a consequence of Mn(II) carbonate complexation. The buffers, overall, reveal a competition between OH^- and CO_3^{2-} ligands in forming Mn(II) complexes. The equilibrium $\text{Mn}(\text{OH})_2(\text{aq}) + \text{CO}_3^{2-} \leftrightarrow \text{MnCO}_3(\text{aq}) + 2 \text{OH}^-$ illustrates this competition. When CO_3^{2-} is elevated at a given pH, hydroxo species concentrations are suppressed. The P_{CO_2} buffer used in the experiments has higher $[\text{CO}_3^{2-}]$ ($\sim 4 \times 10^{-4}\text{M}$) than the C_T buffer ($\sim 8 \times 10^{-5}\text{M}$) at pH 9.0. Thus the manganese carbonate complex concentrations are relatively higher in the P_{CO_2} buffer.

The Mn(II) species concentration factors (Table 3; Fig. 2) are key quantities for the use of expressions (9) and (10) for prediction from theory or for fitting of observed rates to extract species oxidation rate constants.

4. APPLICATION OF THE SPECIES KINETIC MODEL

4.1. Comparison of Outer-Sphere Model Predictions with Kinetic Observations

The elementary steps for reaction between Mn(II) species and molecular oxygen assessed by combining DFT molecular orbital calculations with Marcus theory, and their associated second-order rate constants ($\text{M}^{-1}\text{s}^{-1}$) at zero ionic strength (Rosso and Morgan, 2002) are



By inserting these theoretical values for the $k_{i,\text{OS}}$ in Eqn. 9 together with the a_{ij} values from Table 3 for the fifteen experiments, predicted values of the oxidation rate constants, $k_{j,\text{pred}} = \sum a_{ij} k_{i,\text{OS}}$ can be evaluated for the contributions of Mn^{2+} , MnOH^+ , and $\text{Mn}(\text{OH})_2$ species (outer-sphere rate constant predictions for Mn(II) carbonate species have not yet been made). The results of the calculations are presented in Figure 3, in which experimental and predicted values are compared over the pH range of the experiments. Observed rate constants are approximately four to five orders of magnitude greater than those predicted from the outer-sphere model. (It is noted that the difference persists for experiments in NH_3 buffers, where only the Mn(II) hydrolysis species are involved.)

Table 3. Species fractions^a of Mn(II) in solution for kinetic experiments, 25°C.

Solution	pH	Mn ²⁺	MnOH ⁺	Mn(OH) ₂ ¹	Mn(OH) ₃ ⁻	Mn(NH ₃) ₂ ²⁺	Mn(NH ₃) ₃ ²⁺	MnCO ₃ ⁰	Mn(CO ₃) ₂ ²⁻	MnHCO ₃ ⁺	MnOHCO ₃ ⁻	MnX ^b
Ammonia 10 mM	9.3	9.15E-01	3.66E-02	1.83E-04	9.15E-08	4.73E-02	7.73E-04	0	0	0	0	0
	9.2	9.27E-01	2.97E-02	1.17E-04	4.65E-08	4.26E-02	6.20E-04	0	0	0	0	0
	9.0	9.48E-01	1.90E-02	4.75E-05	1.19E-08	3.31E-02	3.65E-04	0	0	0	0	0
C _r ^c	9.0	4.22E-01	8.43E-03	2.12E-05	5.32E-09	0	0	5.33E-01	8.46E-04	8.45E-03	2.67E-03	0
P _{CO2} ^d	9.25	2.23E-01	4.98E-03	1.77E-05	9.95E-09	0	0	6.60E-01	1.24E-02	7.41E-03	7.93E-02	0
	9.04	4.43E-01	6.11E-03	1.34E-05	4.65E-09	0	0	5.01E-01	3.57E-03	9.07E-03	3.71E-02	0
	8.95	5.49E-01	6.15E-03	1.10E-05	3.08E-09	0	0	4.09E-01	1.92E-03	9.17E-03	2.46E-02	0
Seawater ^e	8.67	5.05E-01	2.97E-03	3.49E-06	8.18E-10	0	0	8.84E-02	2.44E-04	3.00E-03	3.13E-03	0.397
	8.62	5.10E-01	2.67E-03	2.80E-06	5.87E-10	0	0	8.00E-02	2.01E-04	3.06E-03	2.55E-03	0.402
	8.62	5.10E-01	2.67E-03	2.80E-06	5.87E-10	0	0	8.00E-02	2.01E-04	3.06E-03	2.55E-03	0.402
	8.46	5.23E-01	1.90E-03	1.38E-06	1.99E-10	0	0	5.82E-02	1.02E-04	3.19E-03	1.26E-03	0.412
	8.40	5.28E-01	1.67E-03	1.05E-06	1.33E-10	0	0	5.11E-02	7.87E-05	3.23E-03	9.50E-04	0.416
	8.20	5.38E-01	1.08E-03	4.28E-07	3.40E-11	0	0	3.33E-02	3.25E-05	3.33E-03	3.99E-04	0.424
	8.16	5.40E-01	9.82E-04	3.57E-07	2.63E-11	0	0	3.07E-02	2.76E-05	3.36E-03	3.35E-04	0.425
	8.03	5.44E-01	7.34E-04	1.98E-07	1.06E-11	0	0	2.31E-02	1.55E-05	3.42E-03	1.85E-04	0.429

^a The species fraction for Mn²⁺ is [Mn²⁺]/[Mn(II)]_T and so on for each species.^b MnX = MnCl⁺ + MnSO₄ + MnF⁺; the percentages of MnX at pH 8.16 are 88% MnCl⁺, 12% MnSO₄, and ~0.02% MnF⁺.^c Closed system with 3.6 mM dissolved inorganic carbon.^d Open solution with P_{CO2} of 1.42E-04 atm.^e California coastal seawaters from Monterey or Santa Barbara (approximated as closed systems).

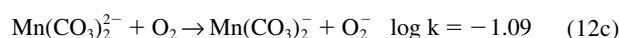
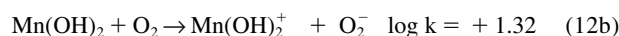
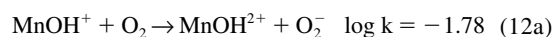
This comparison of experimental rate constants with those predicted on the basis of Marcus theory for outer-sphere paths supports the prediction of Luther (1990) that oxidation of Mn(II) species is more likely to occur via an inner-sphere path, promoted by OH-assisted electron transfer from the Mn²⁺ center to coordinated O₂.

4.2. Fit of the Experimental Data to the Species Kinetic Model

Expression (10) is the basis for fitting the fifteen experimental rate constants to obtain rate constants for Mn(II) reactive species. The observed values of $k_{j,app}/4$ span more than two orders of magnitude. To avoid giving undue weight to the largest values, the regression was carried out using common logarithms of $k_{j,app}/4$ and $k_{j,fit} = \sum k_{i,fit} a_{ij}$. The sum of squares of the residuals, $\log(k_{j,app}/4) - \log k_{j,fit}$, was minimized by using the Solver tool in the Excel application of Microsoft Office. (Because of the nonlinear character of the residuals, it was found necessary to employ several different sets of initial assumptions for the minimization computations to assure global minima.)

Eight species were included in the data fits (Table 3). (Species Mn(NH₃)₂²⁺ and Mn(NH₃)₃²⁺ were omitted on the basis of preliminary rate observations; “MnX” species were omitted on the basis of analogy to experiments with Fe(II) and O₂ (Sung and Morgan, 1980; King, 1998). Each of the eight species was first examined singly in least-squares fitting to estimate its potential contribution. Several pairs of potential contributors were then employed in succeeding fits. “Triplets” of promising species were next examined. This process yielded the species MnOH⁺, Mn(OH)₂, Mn(OH)₃⁻, Mn(CO₃)₂²⁻, and MnOHCO₃⁻ as candidates for detailed examination. It was found that the species Mn(OH)₃⁻ yielded a poor fit to the experimental rates in all combinations with the other species. The low sums of squares of residuals were obtained with three groups: (a) MnOH⁺, Mn(OH)₂, and Mn(CO₃)₂²⁻; (b) MnOH⁺, Mn(OH)₂, and MnOHCO₃⁻; and (c) MnOH⁺, Mn(OH)₂, Mn(CO₃)₂²⁻, and MnOHCO₃⁻. Groups (a) and (c) are nearly indistinguishable from one another on the basis of their least-squares values. The degree of covariance between the species fractions of Mn(CO₃)₂²⁻ and the MnOHCO₃⁻ species is high, with a linear-correlation coefficient $r = 0.960$ (Bevington and Robinson, 2002). The linear-correlation coefficient for the species fractions of Mn(OH)₂ and Mn(CO₃)₂²⁻ is 0.630, indicating a lesser degree of covariance. The choice of group (a) is favored in view of the high covariance within group (c). Details of the fitting exercise for the species MnOH⁺, Mn(OH)₂, and Mn(CO₃)₂²⁻ are given in Table 4. The minimum sum of squares of residuals (logarithms) was 0.31174. (The corresponding sum of squares of the arithmetic residuals, $k_{app}/4 - k_{fit}$, was 4.3E-06.)

The elementary reactions and their rate constants from the fit are



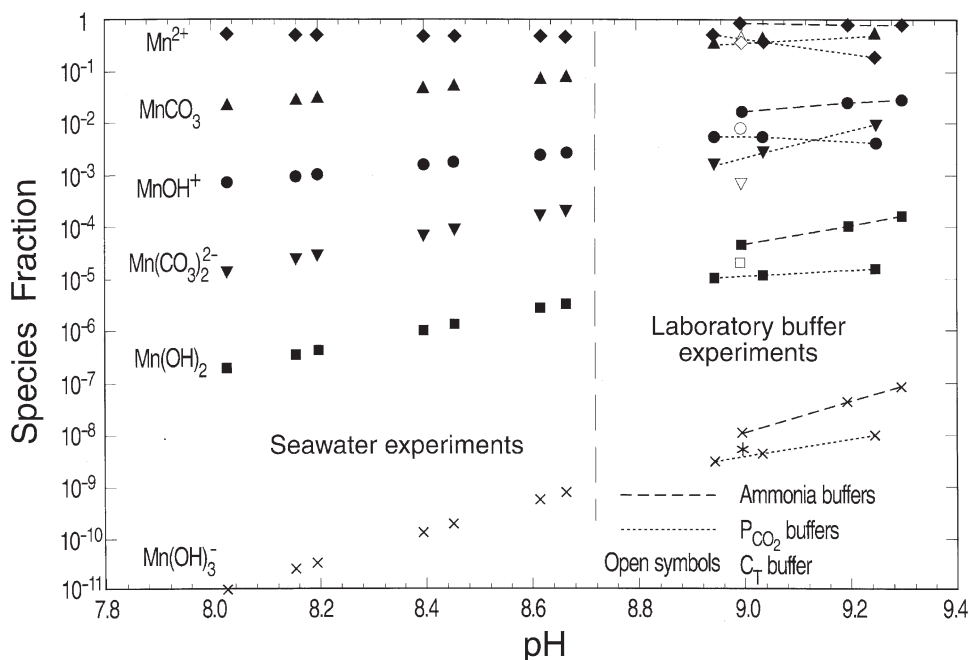


Fig. 2. Species concentration fractions for Mn(II) in the experimental solutions, 25°C. (Data from Table 3. Not all species are shown.)

Figure 4 compares observed and fit values of the rate constants for fifteen experiments. The *inset* shows a log linear regression plot for the experimental and fit rate constants. (The multiple regression coefficient, R^2 , is 0.965.) Agreement between experiments and fits is encouraging, in considering that the results

extend over different laboratory buffers and seawater and span the pH range 8.03 to 9.30.

Some caveats: The carbonate complex formation constants for Mn(II) have not been studied extensively. The constants for these species used here are our estimates (Table 2). There is

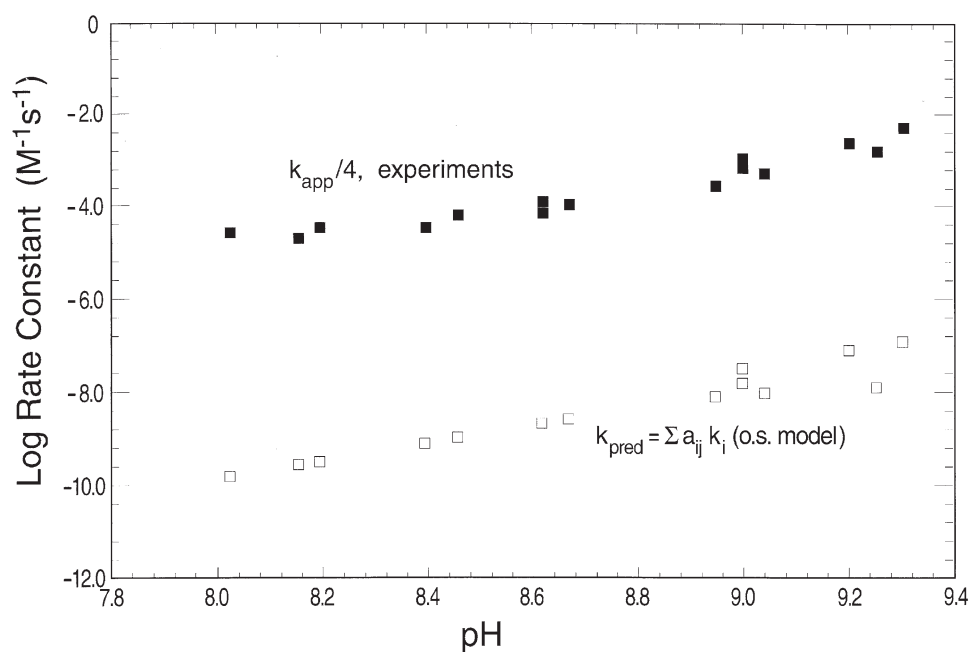


Fig. 3. Experimental values of $k_{j,app}/4$ compared to values predicted on the basis of Marcus outer-sphere theory for electron transfer, 25°C. Predicted one-electron O_2 oxidation rate constants for species Mn^{2+} , $MnOH^+$, and $Mn(OH)_2$ are from Rosso and Morgan (2002). See Eqn. 11 for the k_i values.

Table 4. Fit of proposed rate expression to experimental data^a, 25°C.

Solution	pH	$k_{j,app}/4^b$	$\text{Log}(k_{j,app}/4)$	$k_{j,fit}^c$	$\text{Log } K_{j,fit}$	$(\text{Log}(k_{j,app}/4) - \text{log} k_{j,fit})^2$
Ammonia	9.3	6.30E-03	-2.201	4.43E-03	-2.354	0.02344
	9.2	3.05E-03	-2.516	2.94E-03	-2.532	0.00028
	9.0	8.13E-04	-3.090	1.31E-03	-2.884	0.04236
C_T	9.0	1.19E-03	-2.924	6.52E-04	-3.186	0.06874
	9.25	1.95E-03	-2.710	1.47E-03	-2.833	0.01516
	9.04	4.80E-04	-3.237	6.74E-04	-3.172	0.00422
Seawater	8.95	3.08E-04	-3.511	4.89E-04	-3.311	0.04006
	8.67	1.21E-04	-3.918	1.42E-04	-3.848	0.00491
	8.62	8.32E-05	-4.080	1.19E-04	-3.924	0.02432
	8.62	1.38E-04	-3.860	1.19E-04	-3.924	0.00416
	8.46	7.05E-05	-4.152	6.86E-05	-4.164	0.00014
	8.40	3.68E-05	-4.434	5.60E-05	-4.252	0.03323
	8.20	3.68E-05	-4.434	2.95E-05	-4.531	0.00944
	8.16	2.20E-05	-4.658	2.59E-05	-4.586	0.00514
	8.03	2.72E-05	-4.566	1.75E-05	-4.756	0.03615
						$\Sigma = 0.31174^d$

^a The species rate constants obtained by the fit are: MnOH^+ , 1.66E-02; $\text{Mn}(\text{OH})_2$, 2.09E + 01; and $\text{Mn}(\text{CO}_3)_2^{2-}$, 8.13E-02 ($\text{M}^{-1}\text{s}^{-1}$).

^b The experimental rate constant reexpressed as $k_{j,app}/4$ for comparison with $k_{j,fit}$.

^c $k_{j,fit} = \Sigma k_{i,fit} a_{ij}$.

^d Sum of squares of residuals for log-transformed experimental and fit constants.

uncertainty about the stability of the species MnOHCO_3^- (Section 3.2.1). Omission of this species causes an approximate increase in all other species fractions of 3%. The resulting effect on the fit species fractions is small. As mentioned in Section 3.2.1., the species fraction for chloride ion, Cl^- , was computed a second time for the seawater experiments, revising the stability constant in seawater downward from the value of $10^{0.06}$ used in obtaining Table 3 to a value of $10^{-0.3}$. All other species fractions in seawater were thereby increased by $\sim 25\%$, and the resulting fit species rate constants for all experiments

were affected as follows: $k_{\text{Mn}(\text{OH})_2} = 2.15 \times 10^1$, $k_{\text{Mn}(\text{CO}_3)_2} = 8.09 \times 10^{-2}$, and $k_{\text{MnOH}} = 1.00 \times 10^{-2}$ ($\text{M}^{-1}\text{s}^{-1}$). The fit species rate constant appreciably affected by choice of the lower stability constant for MnCl^+ was that of MnOH^+ ($\sim 39\%$ decrease). A conclusive value of K_{MnCl} is needed to decide on this rate constant. We are inclined to favor the smaller value of K_{MnCl} , and hence a smaller result for k_{MnOH} .

Only one plausible set of Mn(II) hydrolysis constants is available. The fit to experimental data depends on the *product* $k_i a_{ij}$. Uncertainties in species fractions may result from errors

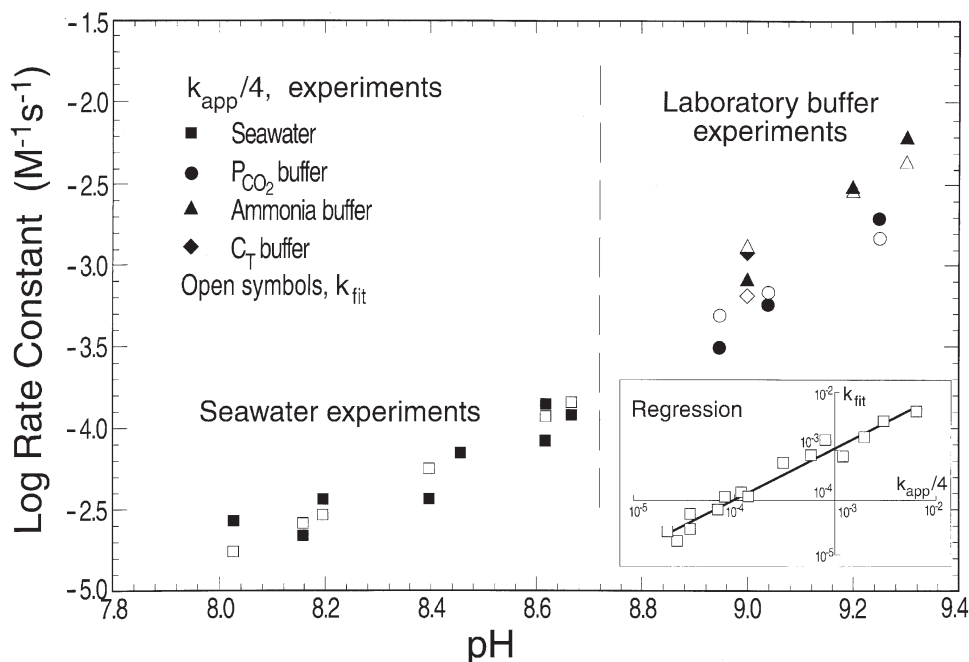


Fig. 4. Results of multiple linear regression of experimental rate constants vs. $k_{j,fit} = \Sigma k_{i,fit} a_{ij}$. (25°C) Two values are shown for each experimental system pH: the $k_{j,app}/4$ of *experiments* and the $k_{j,fit}$ calculated with *best-fit* rate constants for species MnOH^+ , $\text{Mn}(\text{OH})_2$, and $\text{Mn}(\text{CO}_3)_2^{2-}$. The inset shows the regression of $\log k_{j,fit}$ (ordinate) vs. $k_{j,app}/4$ (abscissa).

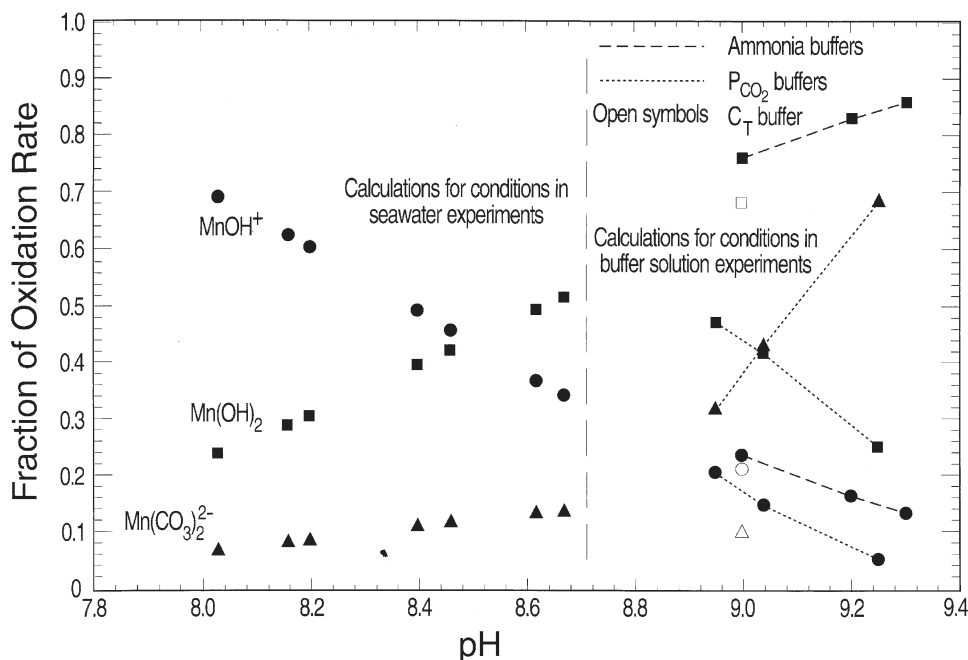


Fig. 5. Fraction of the total fit oxidation rate computed from the species kinetic rate expression with three reactive species (25°C). The fraction is obtained from the expression $f_{i,j} = k_{i,fit} a_{ij} / k_{j,fit}$.

in pH measurements, limitations of the equilibrium constants, and precision in concentrations of solution components (e.g., C_T , P_{CO_2} , salts). The uncertainties in the species rate constants of Eqn. 12a to 12c are expected to be at least as great as those of the experimental rate constants, $k_{app}/4$, possibly somewhat greater. Uncertainties of perhaps 25% can be associated with rate species rate constants.

4.3. Influence of Ionic Strength

The activity coefficients of all ionic species and dissolved gases depend on solution ionic strength, and hence the concentration equilibrium constants are also so dependent. Thus, there is a significant influence of ionic strength on the species concentration factors. Values of $k_{j,app}$ are significantly affected in seawater because of lower O_2 solubility. The experimentally derived species rate constants (Eqn. 12) are envisioned as resulting from three steps: (1) a rapid equilibrium between $O_2(aq)$ and an Mn(II) species, (2) bond formation between O_2 and the Mn^{2+} center, and (3) an ensuing electron transfer step from Mn(II) to bound O_2 . Because O_2 is neutral, no influence of ionic strength on these three steps is predicted. In predicting *outer-sphere* oxidation rates for Mn(II) species by O_2 , Rosso and Morgan (2002) identified a preequilibrium constant, K_i^{pre} , and an electron transfer rate constant, k_i^{et} , with their product, $K_i^{pre} k_i^{et}$, being the predicted species rate constant of oxidation, $k_{i,os}$. (The equilibrium constant for the prior equilibrium between $O_2(aq)$ and any of the Mn(II) species is a function of separation distance, but not a function of ionic strength (Morel and Hering, 1993).) In Marcus theory, ionic strength does affect both the free energy of the overall redox reaction (ΔG°) and the work required to separate O_2^- and charged product species, e.g., $MnOH^{2+}$ to bulk solution (w_p).

4.4. Species Contributions to Total Mn(II) Oxidation Rates

The rate constants of Eqn. 12, together with the species fractions in Table 3, allow calculation of the fraction of the total Mn(II) oxidation rate attributable to the species $MnOH^+$, $Mn(OH)_2$, and $Mn(CO_3)_2^{2-}$. The fraction of the total rate in solution j for species i , f_{ij} , is obtained from the expression:

$$f_{i,j} = k_{i,fit} a_{ij} / \sum k_{i,fit} a_{ij} = k_{i,fit} a_{ij} / k_{j,fit} \quad (13)$$

where the $k_{j,fit}$ are represented by the open symbols in Figure 4. Figure 5 displays the fraction of total Mn(II) + O_2 rate obtained from the species kinetic model.

It is seen that the $MnOH^+$ species is most important at the lower pH range of the seawater experiments, and that its fractional contribution declines steadily throughout the pH range of the seawater and buffer experiments. The decline with pH is more rapid in the P_{CO_2} buffer (compare the NH_3 buffer). The $Mn(OH)_2$ species contribution to the total rate increases steadily in the seawater series. Notice that in the NH_3 buffer, there is a striking elevation of the $Mn(OH)_2$ rate fraction in comparison to that in seawater. This is a consequence of the appreciable $MnCO_3$ species fraction in seawater, which suppresses $Mn(OH)_2$. The importance of the $Mn(OH)_2$ species is diminished sharply in the P_{CO_2} buffer, and there is a correspondingly greater contribution of $Mn(CO_3)_2^{2-}$ to the oxidation rate. Figure 5 illustrates two opposing consequences of speciation: (1) a decrease in rate caused by diminished concentration fractions of some reactive species, and (2) an increase in rate resulting from greater concentrations of other reactive species.

5. CONCLUSIONS

The available experimental observations on oxidation of Mn(II) by molecular O₂ in solution at 25°C yield half-lives for Mn(II) ranging from 350 days to 1 d over the interval from pH ~8.0 to pH ~9.3, respectively (P_{O2} = 0.21 atm). Normalization of the first-order rate constant, k_{j,1}, to unit molar concentration of dissolved O₂ yields the pseudo second-order rate constant, k_{j,app} = k_{j,1}/K_HP_{CO2}, the kinetic parameter of interest in comparing observations with results of a species kinetic model. The kinetic model comprises a set of elementary reactions in parallel, each of the form Mn(II)species + O₂ → Mn(III)species + O₂⁻. The predicted rate of oxidation for all Mn(II) species is k_{pred,j} = Σk_i a_{ij}, in which k_i is a species oxidation rate constant (M⁻¹s⁻¹) and a_{ij} is the fraction of the *i*th species in the *j*th aqueous solution. Rates of Mn(II) disappearance and rate of oxidation are related by k_{app,j} = 4 k_{pred,j}.

Application of the species kinetic model in a predictive mode incorporates theoretical values for the species rate constants together with species fractions of a system. The set of oxidation rate constants for the species Mn²⁺, MnOH⁺, and Mn(OH)₂, based upon molecular orbital computations and the Marcus theory for outer-sphere electron transfer (Rosso and Morgan, 2002), was combined with the Mn(II) species fractions of fifteen experimental systems (Table 3) to compute k_{pred,j} values for Mn²⁺, MnOH⁺, and Mn(OH)₂. Predicted rate constants are *lower* than the observed constants by about four to five orders of magnitude, supporting a prediction by Luther (1990) that an inner-sphere path is to be expected for Mn(II) + O₂.

A least-squares fit of fifteen experimental values of k_{j,app} to the species kinetic model yields reasonable agreement between k_{j,app} and 4 Σk_{i,fit} a_{ij} with three reactive Mn(II) species. The regression coefficient of the log k_{j,app}/4 vs. log Σk_{i,fit} a_{ij} plot is 0.965. The values of k_{i,fit} for the required species of the fit are: k_{Mn(OH)2} = 2.09 × 10¹, k_{Mn(CO3)2} = 8.13 × 10⁻², and k_{MnOH} = 1.66 × 10⁻² (M⁻¹s⁻¹). (Refer to Section 4.2. for discussion of effects of uncertainty about MnCl⁺ stability constant on fit rate constants.)

5.1. Comparison of Mn(II) and Fe(II) Oxidation Kinetics in Solution

It has long been of aqueous geochemical interest to compare rates of Mn(II) and Fe(II) oxidation by dissolved oxygen. Table 5 compares the fit species rate constants of the present work with those from King's earlier findings on Fe(II) + O₂ (King, 1998). A comparison of the fit constants with the outer-sphere predictions of Rosso and Morgan (2002) is also included. Several significant features of the kinetics under consideration are revealed by the information in Table 5. An earlier qualitative awareness of the slowness of Mn(II) reaction with O₂, relative to that of Fe(II) in natural water, is made quantitative through these species rate constant comparisons. Why do Fe(II) and Mn(II) oxidation rates with O₂ differ greatly? The fundamental physico-chemical reasons are to be found in: (i) the M-O bond lengths of the respective oxidized and reduced species, (ii) a large difference between the strengths of Fe(H₂O)₆³⁺ and Mn(OH)₆³⁺ as acids, and (iii) the difference in electronic structure between Fe²⁺ and Mn²⁺. Removal of an electron from an e_g orbital of Mn²⁺ decreases the bond lengths

Table 5. Rate constants for Mn(II) and Fe(II) one-electron oxidation by O₂ (M⁻¹s⁻¹).

Species i	25°C	
	k _{i,os} ^a	k _{i,fit} ^b
Mn ²⁺	1.6 × 10 ⁻¹⁸	<1 × 10 ⁻¹⁰
Fe ²⁺	1.6 × 10 ⁻⁶	1.0 × 10 ⁻⁶
MnOH ⁺	6.3 × 10 ⁻¹⁰	1.66 × 10 ⁻²
FeOH ⁺	2.0 × 10 ⁻²	6.3
Mn(OH) ₂	7.9 × 10 ⁻⁴	20.9
Fe(OH) ₂	1.6 × 10 ²	7.9 × 10 ⁵
Mn(CO ₃) ₂ ²⁻	—	8.1 × 10 ⁻²
Fe(CO ₃) ₂ ²⁻	—	6.6 × 10 ⁵

^a Predicted on the basis of Marcus electron transfer rate theory (Rosso and Morgan, 2002).

^b Fe(II) species oxidation rate constants are from King (1998).

in the resulting Mn(III) species greatly (by 17 PM), much more so than for the Fe(II) → Fe(III) change (by 10 PM). The standard reduction potential for Mn³⁺/Mn²⁺ is 1.55 V, whereas that for Fe³⁺/Fe²⁺ is 0.77 V. There is a much greater energy cost of oxidizing an Mn(II) species to its corresponding Mn(III) species than for Fe(II). The standard free energy differences, ΔG°, for a one-electron O₂ oxidation of an Mn(II) species to the corresponding Mn(III) species compared to analogous Fe(II)/Fe(III) couples are, in kJmol⁻¹:

Mn ²⁺ /Mn ³⁺	MnOH ⁺ /MnOH ²⁺	Mn(OH) ₂ /Mn(OH) ₂ ⁺
164	100	34
Fe ²⁺ /Fe ³⁺	FeOH ⁺ /FeOH ²⁺	Fe(OH) ₂ /Fe(OH) ₂ ⁺
90	48	5

These standard reaction free energy differences account for a part of the kinetic barrier to oxidation. The other part has to do with the energy required to reorganize nuclear coordinates (bond lengths, angles) in the reactant precursor complex before the act of electron transfer. The rate constant of an overall electron transfer reaction can be described by (Eqn. 2) k = κZ exp(-ΔG*/RT). The two parts of the energy barrier to electron transfer, ΔG*, are an *intrinsic* contribution, ΔG*_{intr} comprising the reorganization energies required to form the activated complex, and a *thermodynamic* contribution, ΔG° (Sutin, 1968; Marcus, 1997). For the endergonic oxidations (ΔG° > 0) of Mn(II) or Fe(II) species by O₂, the activation barrier must be at least as great as the standard free energy change in going from reactant to product. Slowness of Mn(II) oxidation in comparison to Fe(II) oxidation may be attributable to a difference in thermodynamic barriers, a difference in intrinsic barriers, or both.

As an example, the experimentally derived rate constants for Fe(OH)₂ and Mn(OH)₂ oxidation are 7.9 × 10⁵ and 20.9, respectively (Table 5), and their ratio is 3.8 × 10⁴. Employing k = κZ exp(-ΔG*/RT), and assuming that the values of κ and Z are roughly the same in the two oxidations, we calculate a difference in ΔG* between the two oxidations of 26 kJmol⁻¹, close to the difference in ΔG° for the two oxidations, 29 kJmol⁻¹.

Thus the difference in observed oxidation rates between Fe(OH)₂ and Mn(OH)₂ appears to be dominated by a difference

in thermodynamic barriers rather than a difference in intrinsic barriers.

If a 25°C value of $k_Z \approx 10^{11} \text{ M}^{-1}\text{s}^{-1}$ is assumed, then $\Delta G^* \approx 55 \text{ kJmol}^{-1}$ on the basis of the fit experimental rate constant for Mn(OH)_2 oxidation (Table 5). For Fe(OH)_2 oxidation, the corresponding estimate from experiment is $\Delta G^* \approx 29 \text{ kJmol}^{-1}$. The Marcus theory prediction for *outer-sphere* oxidation of Mn(OH)_2 , $k_{i,OS} = 7.9 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ (Rosso and Morgan, 2002) corresponds to $\Delta G_{OS}^* = 82 \text{ kJmol}^{-1}$, appreciably greater than the experimentally inferred 55 kJmol^{-1} . The outer-sphere prediction reflects a major intrinsic part in the activation barrier ($\Delta G_{OS}^* = 82$, $\Delta G^\circ = 34 \text{ kJmol}^{-1}$). By contrast, the fit experimental constant for Mn(OH)_2 is indicative of a greater thermodynamic part in the activation barrier ($\Delta G_{exp}^* \approx 55$, $\Delta G^\circ = 34 \text{ kJmol}^{-1}$).

Apart from the Mn^{2+} and Fe^{2+} species, the observed species kinetic properties of Mn(II) and Fe(II) oxidations are not accounted for by an outer-sphere mechanism, thereby pointing to the strong likelihood that an inner-sphere pathway is involved. This aspect was addressed in the case of $\text{Fe(II)} + \text{O}_2$ by Rosso and Morgan (2002). Fallab (1967) and Luther (1990) have proposed that the coordination of the hydroxide base to a metal center, e.g., Fe^{2+} or Mn^{2+} , donates negative charge density to the metal that, in turn, assists in electron transfer from the reduced metal center to bound O_2 . For Mn(II) oxidation, it appears that both OH^- and CO_3^{2-} ligands are able to assist inner-sphere electron transfer from Mn^{2+} to O_2 . The relative base strength of ligands $\text{OH}^- > \text{CO}_3^{2-} > \text{NH}_3 > \text{HCO}_3^- > \text{F}^- > \text{SO}_4^{2-} > \text{Cl}^-$, is consistent with these observations on $\text{Mn(II)} + \text{O}_2$ rate enhancement. It was noted by Luther (1990), for the case of $\text{Fe(II)} + \text{O}_2$, that two ligand atoms (other than H_2O) bound to the metal center lower octahedral symmetry better than one.

The patterns of relative reactivity for the common ligands (hydroxide, carbonate, sulfate, and chloride) which complex Mn(II) in the experiments examined here, suggest that the species kinetic model might be usefully extended to include a wider range of ligands, e.g., those with greater stability constants for Mn(II) and/or with a variety of different molecular structures for their Mn(II) complexes. Experimental work with other ligands in natural waters is attractive to identify those which make Mn(II) either less reactive or more reactive with oxygen. A general role of ligands is to alter the species fractions of Mn(II) in water. A specific role is to alter the rate constant, k_i . Influences of different ligands need be analyzed in the context of the species kinetic expression $\sum k_i a_{ij}$. Ligands that lower the reaction rate do so by diminishing the a_{ij} of more reactive species; those that increase reaction rate form species with net increased products $k_i a_{ij}$ contributing to $\sum k_i a_{ij}$. The influence of a ligand on rate of Mn(II) oxidation is expected to be pH dependent. The extent of protonation of an $\text{Mn}^{\text{II}}\text{LH}_n$ complex can affect both complex stability and reactivity.

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