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The oxidation kinetics of Fe(II) in seawater

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Abstract—The oxidation of Fe(II) has been studied as a function of pH (5 to 9), temperature (5 to 45°C), and salinity (0 to 35). The pseudo-first-order rate constant, k_1,

$$-d[\mathrm{Fe(II)}]/dt = k_1[\mathrm{Fe(II)}]$$

in water and seawater was found to be a second degree function of pH over the pH range of 7.5 to 8.5 at 5°C and 6.0 to 8.0 at 25°C. The overall rate constant (k)

$$-d[\mathrm{Fe(II)}]/dt = k[\mathrm{Fe(II)}][\mathrm{O_2}][\mathrm{OH^-}]^2$$

was determined from 5 to 45°C and S = 0 to 35. The results have been fit to an equation of the form ($T = 273.15 + t$°C)

$$\log k = \log k_0 - 3.29 I^{1/2} + 1.52 I$$

where

$$\log k_0 = 21.56 - 1545/T$$

with a standard error = 0.09. The energy of activation for the overall rate constant in water and seawater was 29 ± 2 kJ mol^{-1}.

The values of the rate constant for pure water (k_0) are in good agreement with literature data. The half times for seawater from some previous studies at a pH = 8.0 were slower than our results for Gulf Stream waters. Measurements on Biscayne Bay waters also yield slower half times apparently due to the presence of organic ligands that can complex Fe(II).

INTRODUCTION

REDUCED FORMS OF iron in natural waters can be produced in the pore waters of sediments, in anoxic basin waters, in hydrothermal waters and perhaps in surface waters by photochemical processes. Once this reduced iron, Fe(II), is formed its lifetime in oxygenated waters will be related to the rates of its oxidation. Since Fe(II) can form complexes with the various ligands present in the waters, one would expect these rates to be variable (MILLERO, 1985).

The kinetics of oxidation of Fe(II) have been studied in fresh water (STUMM and LEE, 1961; MORGAN and BIRKNER, 1966; SCHENK and WEBER, 1968; TAMURA *et al.*, 1976; GHOSH *et al.*, 1974; SUNG and MORGAN, 1980; DAVISON and SEED, 1983) and in seawater (KESTER *et al.*, 1975; MURRAY and GILL, 1978; ROEKENS and VAN GRIEKEN, 1983; WAITE and MOREL, 1984). The results for the pseudo-first-order rate constant (k_1)

$$-d[\mathrm{Fe(II)}]/dt = k_1[\mathrm{Fe(II)}] \tag{1}$$

at a given pH and temperature are in good agreement in fresh water (DAVISON and SEED, 1983; LOWSON, 1982). The limited measurements in seawater are also in reasonable agreement. For example, at a pH = 8 the half life times of Fe(II), $t_{1/2} = \ln 2 \cdot k_1^{-1}$, for seawater between 15 to 25°C are between 2 to 3 min. The value of k_1 is strongly dependent upon pH and the general rate law valid over most of the range of natural waters has been found to be (STUMM and LEE, 1961)

$$k_1 = k[\mathrm{OH^-}]^2[\mathrm{O_2}]. \tag{2}$$

The recent measurements of ROEKENS and VAN GRIEKEN (1983) in seawater have shown smaller changes in the pH (or pOH) dependence of k_1 below pH = 6 and above pH = 8.0. Although these results have been questioned (DAVISON, 1984; ROEKENS and VAN GRIEKEN, 1984), the variability in the pH dependence especially between 2 to 8 has been known for some time (LOWSON, 1982).

As discussed elsewhere (MILLERO, 1985), the pH dependence of the speciation of Fe(II) is described by the hydrolysis equilibria

$$\mathrm{Fe^{2+} + OH^- \rightarrow Fe(OH)^+} \tag{3}$$

$$\mathrm{Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2^0} \tag{4}$$

$$\mathrm{Fe^{2+} + 3OH^- \rightarrow Fe(OH)_3^-}. \tag{5}$$

Thus, the oxidation reaction of Fe(II) is composed of several parallel reactions involving the various Fe(II) species, *e.g.*

$$\mathrm{Fe^{2+} + O_2 \xrightarrow{k_{Fe}} Products} \tag{6}$$

$$\mathrm{Fe(OH)^+ + O_2 \xrightarrow{k_{FeOH}} Products} \tag{7}$$

$$\mathrm{Fe(OH)_2 + O_2 \xrightarrow{k_{Fe(OH)_2}} Products} \tag{8}$$

$$\mathrm{Fe(OH)_3^- + O_2 \xrightarrow{k_{Fe(OH)_3}} Products}. \tag{9}$$

The overall rate constant (k) is given by

$$k = k_{\mathrm{Fe}}\alpha_{\mathrm{Fe}} + k_{\mathrm{FeOH}}\alpha_{\mathrm{FeOH}} + k_{\mathrm{Fe(OH)_2}}\alpha_{\mathrm{Fe(OH)_2}} + k_{\mathrm{Fe(OH)_3}}\alpha_{\mathrm{Fe(OH)_3}} \qquad (10)$$

where the values of α_i are the molar fractions of species i in total dissolved iron. These fractions can be calculated from the stepwise association constants for Eqns. 3 to 5. Since $\alpha_{\mathrm{Fe}} \sim 1.0$ from pH 2 to 8 (BAES and MESMER, 1976), the values of α_{FeOH}, $\alpha_{\mathrm{Fe(OH)_2}}$ and $\alpha_{\mathrm{Fe(OH)_3}}$ are proportional, respectively, to $[\mathrm{OH}^-]$, $[\mathrm{OH}^-]^2$ and $[\mathrm{OH}^-]^3$ (MILLERO, 1985). Since strong interactions of Fe^{2+} with some ligands can decrease the rates (MILLERO, 1985), complications can result due to changes in ligand concentrations as a function of pH. For example, the leveling off of the rate in seawater above a pH = 8.3 (ROEKENS and VAN GRIEKEN, 1983) could be due to the formation of FeCO_3^0 (TURNER *et al.*, 1981).

Although the rates of oxidation of Fe(II) in fresh and sea waters have been extensively studied near 25°C, the effect of salinity, temperature, and pH has not been examined thoroughly for seawater and estuarine waters. In this paper we will present results for the effect of pH, salinity, and temperature on the rates of oxidation of Fe(II) in seawater solutions. These results have been used to give rate equations for the oxidation of Fe(II) valid for most natural waters (devoid of large concentrations of organic ligands).

EXPERIMENTAL

Reaction vessel. The reactions were studied in a 500 ml glass thermostatically controlled vessel. The temperature was controlled to ±0.02°C with a Neslab circulating bath. The top of the vessel had an opening for a glass frit used to bubble air-$\mathrm{CO_2}$ mixtures through the solutions. The samples were taken from the vessel with a 10 ml calibrated automatic repipette. A Corning glass pH electrode and an Orion calomel reference electrode were used to monitor the pH with a Beckman pH meter during a run. The solutions were stirred with a magnetic stirrer.

Chemicals. All of the chemicals used were reagent grade. Most of the Fe(II) stock solutions (0.1 m) were prepared with $\mathrm{FeCl_2}$ or $\mathrm{Fe(ClO_4)}$ acidified with HCl. For some of the measurements stock solutions were made with $\mathrm{FeSO_4}$, $\mathrm{FeSO_4(NH_4)_2SO_4}$ and dissolving electrolyte grade iron powder in 0.1 M $\mathrm{HClO_4}$ (SUNG and MORGAN, 1980). The kinetic runs adjusted to the same pH were found to be in agreement using the various stock solutions. Initial concentrations of Fe(II) from 3 to 100 μM gave similar kinetic results. For most of our experiments the initial concentration of Fe(II) was between 20 to 50 μM. The water used in all the experiments was ion exchanged Millipore Super Q (18 MΩ). The seawater used was Gulf Stream water collected off the coast of Miami. The salinity was determined with a Guildline Autosal conductance bridge using the Practical Salinity scale. After filtration through a 0.45 μm filter, the dilute samples were prepared by weight using ion exchanged water.

Iron analysis. The Fe(II) concentrations were determined spectrophotometrically with bathophenanthroline (SUNG and MORGAN, 1980). A 10 ml aliquot was taken from the reaction vessel and quenched with 1 ml of 3.6 m $\mathrm{H_2SO_4}$, 2 ml of 2 m $\mathrm{NH_4F}$, 1 ml of 1% bathophenanthroline and 5 ml of 2 m hexamethylenetetramine. The solution was diluted to 50 ml with ion exchanged water. The absorbance was measured at 510 nm on a Varian spectrophotometer using a 10 cm cell. Beer's law was obeyed from 2 to 100 μM. For seawater samples we also quenched the 10 ml aliquots with 10 ml of ammonium acetate buffer (pH = 4.0) and 1 ml of 1% bathophenanthroline (ROEKENS and VAN GRIEKEN, 1983). The sample was diluted with ion exchanged water and the absorbance was measured at 533 nm. Both analytical procedures gave similar results within experimental error.

Oxygen concentration. All of the measurements were made in solutions saturated with air. The solutions were saturated at a given temperature by bubbling air through them for 30–45 minutes. The molal concentrations of $\mathrm{O_2}$ in the solutions at a given temperature and salinity were calculated from the equations of BENSON *et al.* (1979) and BENSON and KRAUSE (1984). Direct measurements of $\mathrm{O_2}$ using the Winkler technique (CARPENTER, 1965) gave concentrations that agreed with the equations of BENSON *et al.* (1979) and BENSON and KRAUSE (1984) to ±1%.

pH measurements. Since the oxidation of Fe(II) in aqueous solutions is strongly dependent upon pH, (DAVISON and SEED, 1983), great care was taken in controlling and measuring pH. For water and dilute seawater solutions this was done by using bicarbonate-carbon dioxide buffers. As shown by others (STUMM and LEE, 1961; SUNG and MORGAN, 1980; ROEKENS and VAN GRIEKEN, 1983), we found that this buffer system can adequately control the pH to ±0.01 during an experimental run (after the initial adjustment period of about 20 seconds due to the addition of the acidic stock solution). All of the values of pH given in this paper are the average values obtained during a given experimental run. The addition of the stock solutions would instantaneously lower the pH by as much as 0.1 units (depending upon the level of Fe(II) and H^+ in the stock solution). The values during a run agreed on the average to ±0.03 pH units. NBS buffers (phosphate buffer-pH = 7.413 at 25°C) were used to standardize the electrodes and determine the pH in water (0.009 $\mathrm{NaHCO_3}$). These buffers cannot yield reproducible results in seawater due to liquid junctions (DICKSON, 1984; MILLERO, 1986). Therefore, we used TRIS-seawater (0.005 m) buffers (HANSSON, 1973; RAMETTE *et al.*, 1977) to calibrate our electrode system and determine the pH of seawater solutions. The calibrations were made at each salinity and temperature using the $\mathrm{pH_F}$ on the free molal scale (RAMETTE *et al.*, 1977) and the equations of MILLERO (1986). Conversions to the total or seawater scale can be made using values of $\beta_{\mathrm{HSO_4}}$ for the formation $\mathrm{HSO_4^-}$ (MILLERO, 1986). The TRIS buffers are very stable and gave the same emfs to ±0.2 mv for months. Since we also calibrated our electrode at various temperatures using NBS buffers (MILLERO, 1986), it is possible to determine an apparent activity coefficient f_H for H^+ that can be used to relate the $\mathrm{pH_F}$ and $\mathrm{pH_{NBS}}$ scales

$$a'_{\mathrm{H}} = f_{\mathrm{H}}[\mathrm{H}^+]. \qquad (11)$$

This relationship, however, is valid only for our electrode system since f_H is related to variable liquid junction effects (DICKSON, 1984). TRIS buffers must be used to make reliable comparisons to our experimental results.

Since the concentration of free (OH^-) is needed to express the effect of pOH on the rate constant, it was necessary to estimate the pK^*_W for the ionization of water on the free scale

$$K^*_W = [\mathrm{H}^+]_F[\mathrm{OH}^-]_F = K_W(a_{\mathrm{H_2O}}/\gamma^F_{\mathrm{H}}\gamma^F_{\mathrm{OH}}) \qquad (12)$$

where K_W is the thermodynamic dissociation constant, γ^F_i is the free activity coefficient of species i (*i.e.*, not including interactions of H^+ with $\mathrm{SO_4^{2-}}$ and OH^- with Mg^{2+}) and $a_{\mathrm{H_2O}}$ is the activity of water. At 25°C we have estimated the values of γ^F_{H} and γ^F_{OH} at various salinities using Pitzer's equations (PITZER, 1979; HARVIE *et al.*, 1984; MILLERO, 1982). The activity of water can be estimated from similar equations for the osmotic coefficient (PITZER, 1979) or from the thermodynamic properties of seawater (MILLERO and LEUNG, 1976). The estimated and experimentally derived values of $a_{\mathrm{H_2O}}$ are in good agreement. The values of K^*_W calculated in this manner are given in Table 1. The values of K_W for water at a given temperature ($T = 273.15 + t$°C) can be determined from (MILLERO, 1979a)

Table 1. Values of pK_W^* at 25^oC for the Ionization of Water in Seawater on the Free Proton Scale.

S	I^a	$a_{H_2O}/\gamma_H^F\gamma_{OH}^F$	pK_W^*
40	0.830^a	2.3602^b	13.622
35	0.723	2.3351	13.627
30	0.616	2.2975	13.634
25	0.511	2.2381	13.645
20	0.407	2.1630	13.660
15	0.303	2.0567	13.682
10	0.201	1.9108	13.174
7.5	0.151	1.8106	13.737
5	0.100	1.6827	13.769
4	0.080	1.6218	13.785
3	0.060	1.5447	13.806
2	0.040	1.4518	13.833
1	0.020	1.3251	13.873
0.5	0.010	1.2328	13.904
0.25	0.005	1.1661	13.928
0	0	1.0000	13.995

a) $I = 19.9201\ S/(10^3 - 1.00488\ S)$ Millero (1982).

b) Pitzer equations (Millero, 1982) for γ_H^F and γ_{OH}^F and a_{H_2O} from Millero and Leung (1976).

$$\ln K_W = 148.9802 - 13847.26/T - 23.6521 \ln T \qquad (13)$$

which is based on the results of HARNED and OWEN (1958).

The effect of temperature on the values γ_H^F and γ_{OH}^F over a limited temperature range can be estimated from relative partial molal enthalpy $\bar{L}$ and relative partial molal heat capacity $\bar{J}$ data (MILLERO, 1979b). Since the values of $(\gamma_H\gamma_{OH}/a_{H_2O})$ have been experimentally determined for NaCl, KCl and $SrCl_2$ solutions (HARNED and OWEN, 1958), we have elected to determine the temperature coefficients for seawater from these results. This was done by fitting the experimental values to Pitzer's equations in the form (m is molality)

$$\ln (\gamma_H\gamma_{OH}/a_{H_2O}) = 2f^\gamma + B^0 m + B^1 f^1 + Cm^2 \qquad (14)$$

where the Debye-Hückel term is given by

$$f^\gamma = -A^\phi[I^{1/2}/(1+1.2I^{1/2}) + 1.667 \ln (1+1.2I^{1/2})] \qquad (15)$$

and $f^1 = 1 - (1 + 2I^{1/2} - 2I)\exp(-2I^{1/2})$. The parameters B^0, B^1 and C were determined from the experimental values of $(\gamma_H\gamma_{OH}/a_{H_2O})$. The values of A^ϕ from 0 to 50°C (AMANTHASWAMY and ATKINSON, 1984) were fit to the equation (standard error $= 6 \times 10^{-5}$)

$$A^\phi = -5.8901 + 228.2338/T + 0.968144 \ln T. \qquad (16)$$

The parameters B^0, B^1 and C for all of the salts were fit to equations of the form

$$B^0 = a + b/T + c \ln T \qquad (17)$$

$$B^1 = d \qquad (18)$$

$$C = e + f/T. \qquad (19)$$

The temperature coefficients (b, c and f) for seawater were estimated from values for the various salts using the composition of seawater (MILLERO, 1982) and equations of the form

$$b = m_{Na}b_{NaCl} + m_K b_{KCl} + (m_{Sr} + m_{Mg} + m_{Ca})b_{SrCl}. \qquad (20)$$

These temperature coefficients were combined with the 25°C parameters for seawater to give

$$B^0 = 20.6365 - 945.556/T - 3.00298 \ln T \qquad (21)$$

$$B^1 = 0.18062 \qquad (22)$$

$$C = -0.05346 + 17.6216/T. \qquad (23)$$

The values of $\gamma_H\gamma_{OH}/a_{H_2O}$ calculated from Eqns. (14), (15), (16), (21), (22) and (23) from 0 to 50°C for S = 35 seawater are given in Table 2. The results were found to be in excellent agreement with the values estimated using

$$\log (\gamma_H\gamma_{OH})_T = \log (\gamma_H\gamma_{OH})_{298} + Y\bar{L}_{298} + Z\bar{J}_{298} \qquad (24)$$

where the coefficients Y and Z at various temperatures are given elsewhere (MILLERO, 1979b). The values of $\bar{L}_{298} = 1379$ J mol^{-1} and $\bar{J}_{298} = 48.2$ J mol^{-1} K^{-1} were determined using the specific interaction model (MILLERO, 1979b).

RESULTS AND DISCUSSION

pH dependence. In our first series of measurements we determined the pseudo-first-order rate constant (k_1 in units of min^{-1}) in water and seawater as a function of pH. The results for water and seawater at 5 and 25°C are given in Tables 3 and 4 and shown in Figs. 1 and 2. Over a limited pH range the results can be fitted to the linear equation

$$\log k_1 = a_0 + a_1\text{pH}. \qquad (25)$$

Table 2. The Effect of Temperature on Activity Product $(\gamma_H\gamma_{OH}/a_{H_2O})$ For S = 35 Seawater.

Temp.	a	b	Δ
0^oC	0.4412	0.4403	0.0009
5	0.4398	0.4393	0.0005
10	0.4378	0.4375	0.0003
15	0.4351	0.4350	0.0001
20	0.4319	0.4320	0.0001
25	0.4281	0.4281	-
30	0.4239	0.4239	0
35	0.4193	0.4192	0.0001
40	0.4143	0.4140	0.0003
45	0.4090	0.4085	0.0005
50	0.4034	0.4028	0.0006

a) From NaCl, KCl, and $SrCl_2$ data (Harned and Owen, 1958)

b) From $\bar{L}_{25}$ and $\bar{J}_{25}$ data (Millero, 1979b) and a_{H_2O} data (Millero and Leung, 1976). It should be pointed out that the values of a_{H_2O} do not change much with temperature (a_{H_2O} = 0.9815 and 0.9812, respectively, at 0 and 50^oC).

Table 3. The Effect of pH on the Pseudo First Order Rate Constant for the Oxidation of Fe(II) in Water[a].

5°C		25°C			
pH_{NBS}	$-\log k_1$	pH_{NBS}	$-\log k_1$	pH_{NBS}	$-\log k_1$
7.357	2.404	4.973	4.943	7.129	1.170
7.502	2.123	5.007	5.023	7.144	1.334
7.611	1.807	5.232	4.823	7.330	0.962
7.723	1.636	5.295	4.618	7.416	0.617
7.845	1.361	5.450	4.282	7.527	0.384
7.917	1.217	5.502	4.196	7.527	0.345
7.973	1.047	5.707	3.915	7.601	-0.093
8.036	1.024	5.868	3.683	7.640	-0.065
8.080	0.806	6.015	3.313	7.727	-0.282
8.096	0.737	6.025	3.387	7.743	-0.361
8.197	0.599	6.181	3.087	7.748	-0.277
8.243	0.479	6.282	2.796	7.816	-0.364
8.328	0.356	6.335	2.876	7.997	-0.638
8.384	0.304	6.386	2.671	8.089	-0.712
8.484	0.105	6.490	2.543	8.202	-0.696
		6.594	2.438	8.347	-0.872
		6.694	2.292	8.391	-0.915
		6.801	1.892	8.685	-0.981
		6.882	1.838	8.869	-1.072
		6.996	1.541		

a) k_1 in units of min^{-1} (for 0.009 m $NaHCO_3$).

Table 4. The Effect of pH_F on the Pseudo First Order Rate Constant for the Oxidation of Fe(II) in Seawater[a].

5°C		25°C			
pH_F	$-\log k_1$	pH_F	$-\log k_1$	pH_F	$-\log k_1$
7.415	2.890	4.998	4.503	7.300	1.825
7.600	2.766	5.237	4.355	7.448	1.310
7.650	2.754	5.508	4.258	7.590	1.176
7.753	2.494	5.756	4.161	7.739	0.988
7.756	2.532	5.878	4.259	7.776	0.785
7.772	2.557	5.904	4.172	7.930	0.506
7.844	2.224	5.983	4.334	7.998	0.198
7.884	2.202	6.113	3.917	8.006	0.143
7.995	1.916	6.245	3.873	8.038	0.095
7.997	1.859	6.588	3.093	8.302	-0.322
8.045	1.810	6.833	2.684	8.571	-0.655
8.098	1.845	6.842	2.691	8.804	-1.008
8.209	1.696	6.982	2.616	8.929	-0.857
8.238	1.521	7.000	2.390		
8.292	1.441	7.186	2.147		
8.446	1.087	7.202	1.977		
8.515	0.920				
8.607	0.775				
8.695	0.648				
8.790	0.466				
8.961	0.210				
8.998	0.116				
9.011	-0.0998				
9.149	-0.3114				
9.312	-0.576				

a) k_1 in units of min^{-1} (for S = 35 seawater).

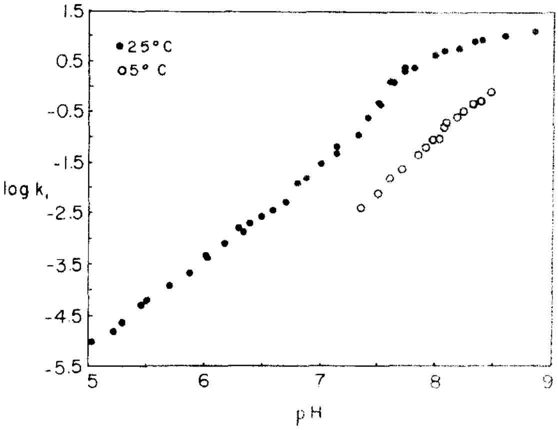

FIG. 1. Pseudo-first-order rate constant for oxidation of Fe(II) in water (0.009 m $NaHCO_3$) as a function of pH (NBS).

The coefficients for this equation are given in Table 5. The results at 5° over the pH range of 7.5 to 9.0 yielded slopes of $a_1 = 2.08 \pm 0.04$ and 1.98 ± 0.03, respectively, for water and seawater with standard errors of 0.06 to 0.08 in log k_1. At 25°C over the pH range of 6 to 8, the slopes are $a_1 = 2.13 \pm 0.14$ and 1.87 ± 0.15, respectively, for water and seawater with standard errors of 0.14 to 0.21 in log k_1. Our results clearly show (Table 5) that a second degree pH dependence is obeyed over a reasonable pH range in agreement with earlier studies (STUMM and LEE, 1961; ROEKENS and VAN GRIEKEN, 1983; DAVISON and SEED, 1983). The larger errors at 25°C are due in part to the non-linear behavior of log k_1 over the entire pH range of the measurements. To fit the total data a more complicated pH dependence is found. The 25°C results have been fitted to the equations

$$\log k_1(H_2O) = 36.525 - 21.451\text{pH} + 3.4951\text{pH}^2 - 0.172083\text{pH}^3 \quad (26)$$

$$\log k_1(SW) = 56.809 - 28.199\text{pH} + 4.1331\text{pH}^2 - 0.18755\text{pH}^3 \quad (27)$$

with standard errors, respectively, of $\sigma = 0.16$ and 0.15 in log k_1.

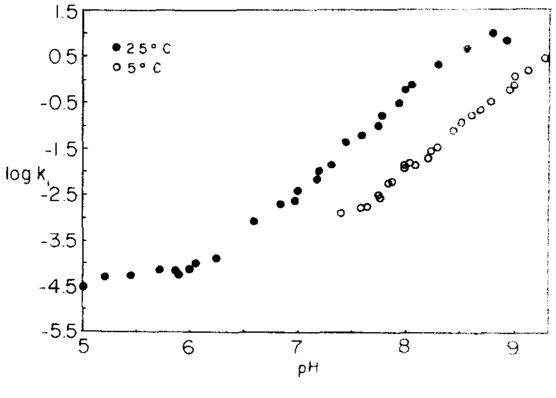

FIG. 2. Pseudo-first-order rate constant for oxidation of Fe(II) in $S = 35$ seawater as a function of pH_F.

Table 5. Coefficients for the pH Dependence of k_1 for the Oxidation of Fe(II).

Temp.	Media	a_0	a_1	pH Range
5°C	Water^a	-17.697 ± 0.06	2.08 ± 0.04	7.4 - 8.5
	Seawater^b	-17.809 ± 0.08	1.98 ± 0.03	7.6 - 9.3
25	Water^a	-16.331 ± 0.14	2.13 ± 0.14	6 - 8
	Seawater^b	-15.391 ± 0.21	1.87 ± 0.15	6 - 8
20.5	Water^c	-15.39 ± 0.05	2.04 ± 0.05	6.4 - 7.1
15	Seawater^d	-17.16 ± 0.31	2.19 ± 0.28	6.7 - 8.0
10	Lake Water^e	-12.25	1.42 ± 0.78	6.8 - 7.2

a) 0.009m $NaHCO_3$
b) S = 35.00
c) From Stumm and Lee (1961), 0.03 - 0.04M $NaHCO_3$ (for k_1/P_{O_2}).
d) From Roekens and Van Grieken (1983), S = 32 (for k_1/P_{O_2}).
e) From Davison and Seed (1983).

The lower pH dependence between pH 5 to 6 is related to the slower oxidation of the $Fe(OH)^+$ species (MILLERO, 1985). The smaller change in log k_1 at higher values of pH 8 to 9 may be related to the precipitation of $Fe(OH)_2$, or the slower oxidation of ion pairs $Fe(OH)_3^-$ or $FeCO_3$ compared to $Fe(OH)_2^0$. Since the rates are quite fast above pH = 8.5, it is difficult to obtain reliable results by the methods used in this study. Stopped flow methods are needed to obtain reliable results above a pH = 8.5 at 25°C.

Most of the pH studies made have utilized the CO_2-HCO_3^- buffer system. Results of log k_1 in TRIS and borate buffers (Fig. 3) show a similar second degree function of pH, but are depressed apparently due to the formation of complexes of Fe^{2+} with TRIS and $B(OH)_4^-$ that have a slower rate of oxidation. The depression of log k_1 in seawater solutions has been explained in a similar manner (MILLERO, 1985). The $FeCl^+$ and $FeSO_4$ species have slower oxidation rates than $Fe(OH)_2$. We are presently making measurements at high pH in borate buffers to see if log k_1 decreases as in the CO_2-HCO_3^- system. Studies at a fixed pH in $NaClO_4$ + Na*X* solutions are also in progress to examine the decrease in the oxidation rate due to complex formation of Fe^{2+} with various ligands (*X*).

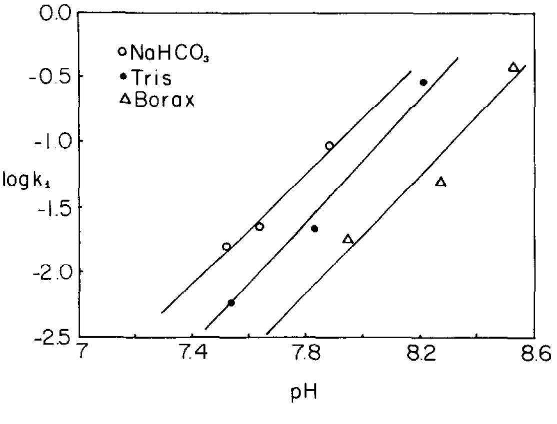

FIG. 3. The oxidation of Fe(II) in dilute buffers at 5°C as a function of pH_F.

Salinity dependence. To determine the effect of salinity on the oxidation of Fe(II) in seawater it is necessary to make corrections for pH or *p*OH and oxygen variations. As discussed earlier, the overall rate equation over a limited pH range is given by

$$-d[Fe(II)]/dt = k[OH^-]^2[O_2][Fe(II)]. \quad (28)$$

Unlike earlier expressions of the rate equation we have expressed the oxygen dependence in terms of the molal concentration, not P_{O_2}. This is necessary due to decreases in concentration of O_2 due to salting out and changes in solubility at various temperatures. It is also necessary to make the measurements in a pH range where the second degree variation is valid. The OH^- concentration refers to the molal concentration devoid of complex formation with Mg^{2+}. This is necessary since the stability constant of $MgOH^+$ is a function of temperature and salinity.

The values of the overall rate constant (*k* in units of mol^{-3} kg H_2O^3 min^{-1}) for the oxidation as a function of salinity at 5 and 25°C are given in Table 6 and shown plotted *versus* ionic strength in Fig. 4. The results are based on at least two measurements at similar values of pH. Within experimental error the salinity de-

Table 6. The Effect of Salinity on the Oxidation of Fe(II) in Seawater.

S	I^a	log k^b 5°C	 25°C
35	0.723	14.36 ± 0.02	14.74 ± 0.03
30	0.616	14.31 ± 0.04	14.77 ± 0.03
25	0.511	14.28 ± 0.05	14.81 ± 0.02
20	0.407	14.37 ± 0.05	14.93 ± 0.01
15	0.303	14.51 ± 0.05	15.04 ± 0.05
10	0.201	14.74 ± 0.06	15.18 ± 0.01
7.5	0.151	14.94 ± 0.05	15.44 ± 0.01
5	0.109	15.05 ± 0.05	15.57 ± 0.06
4	0.089	-	15.66 ± 0.03
3	0.069	15.13 ± 0.05	15.72 ± 0.04
2.5	0.059	-	15.75 ± 0.01
2	0.049	15.33 ± 0.05	15.75 ± 0.01
1	0.029	15.38 ± 0.06	15.88 ± 0.04
0.5	0.019	15.44 ± 0.05	-
0.25	0.014	15.59 ± 0.05	16.03 ± 0.01
0.1	0.011	-	16.08 ± 0.03
0	0.009	15.70 ± 0.05	16.11 ± 0.02

a) 0.009 m $NaHCO_3$ was added to the samples with S = 7.5 to 0 (on pH_F scale).
b) The average based on at least two measurements at each salinity over the pH range of 7.5 $\pm$ 0.5 and 8.0 $\pm$ 0.5, respectively, at 25° and 5°C. Units of mol^{-3} kg H_2O^3 min^{-1}.

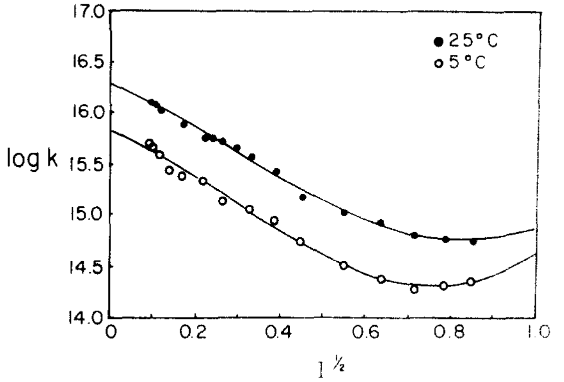

FIG. 4. Oxidation of Fe(II) in seawater *versus* ionic strength at 5 and 25°C.

pendence of k is independent of temperature. The results have been fit to an equation of the form

$$\log k - \log k_0 = -3.29I^{1/2} + 1.52I \qquad (29)$$

with $\sigma = 0.07$ and 0.10, respectively, at 25 and 5°C.

It should be pointed out that the near linear dependence of log k in dilute solutions is a function of the pH scale used. This is demonstrated in Fig. 5. The slope is 1.55 when using the NBS scale ($a_{OH} = K_W/a_H$), while the free scale gives a slope of 2.28. The extrapolated values to pure water are independent of the pH scale used.

Temperature dependence. The effect of temperature on the oxidation of Fe(II) has been determined in water (0.009 m $NaHCO_3$) and seawater ($S = 35$). These measurements were made over a pH range where the second degree variability is obeyed. The effect of temperature on the pseudo-first-order rate constant

$$\partial \ln k_1/\partial T = \Delta H_1^{\ddagger}/RT^2 \qquad (30)$$

are difficult to determine exactly due to the problems of making the measurements at the same pH. If adjustments are made one obtains values of $\Delta H_1^{\ddagger} = 125 \pm 2$ kJ mol^{-1} independent of salinity. This can be compared to a value of 105 ± 25 kJ mol^{-1} obtained by SUNG and MORGAN (1980). This value is related to the effect of temperature on the solubility of O_2, the K_W^* for the ionization of water and the overall rate constant.

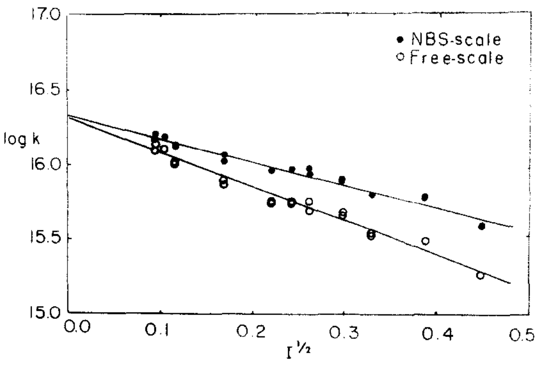

FIG. 5. The effect of ionic strength on the rate of oxidation of Fe(II) using various pH scales.

Table 7. The Effect of Temperature on the Oxidation of Fe(II) in Water and Seawater (S = 35).

	log k[a]	
Temp.	Water[b]	Seawater
5°C	15.78 ± 0.05	14.34 ± 0.08
10	15.79 ± 0.03	14.37 ± 0.07
15	15.99 ± 0.12	14.48 ± 0.12
20	15.99 ± 0.11	14.49 ± 0.04
25	16.07 ± 0.15	14.65 ± 0.10
30	16.06 ± 0.03	14.72 ± 0.07
35	16.24 ± 0.12	14.74 ± 0.09
40	16.28 ± 0.12	14.87 ± 0.08
45	16.30 ± 0.10	14.75 ± 0.12

a) The average based on two or more measurements at each temperature (on pH_F scale).

b) For 0.009 m $NaHCO_3$. Units of mol^{-3} KgH_2O^3 min^{-1}.

Values of log k for the overall rate equation at various temperatures for water and seawater are given in Table 7 and shown plotted *versus* $1/T$ in Fig. 6. The temperature dependent changes in k are much smaller than in k_1 as shown by SUNG and MORGAN (1980). The energy of activation found for the combined data is found to be 29 ± 2 kJ mol^{-1}. This can be compared to a value of 17 ± 13 kJ mol^{-1} found by treating the data of SUNG and MORGAN (1980) in a similar manner. The agreement is within the combined experimental error.

The effect of temperature and salinity on all the measurements made in this study have been fit to the equation

$$\log k = 21.56 - 1545/T - 3.29I^{1/2} + 1.52I \qquad (31)$$

which has a $\sigma = 0.09$. Values of k_1 can be determined from this equation using (BENSON and KRAUSE, 1984)

$$\begin{aligned} \ln [O_2] = &-135.29996 + 1.572288 \times 10^5/T \\ &- 6.637149 \times 10^7/T^2 + 1.243678 \times 10^{10}/T^3 \\ &- 8.62106 \times 10^{11}/T^4 - S(0.020573 \\ &- 12.142/T + 2363.1/T^2) + \ln (1 + 10^{-3}S) \qquad (32) \end{aligned}$$

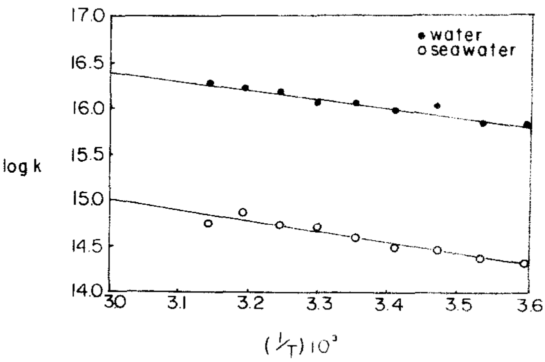

FIG. 6. The effect of temperature on the rate of oxidation of Fe(II) in water and seawater.

Table 8. Comparison of the Values of log k for the Oxidation of Fe(II) in Dilute Solutions.

Temp.	log k[a]	Reference
25°C	16.18 ± 0.05	This study
	16.27 ± 0.15	Davison and Seed (1983)
	16.16 to 16.48	Sung and Morgan (1980)
	16.10 ± 0.1	Morgan and Birkner (1966)
	16.21 ± 0.04	Schenk and Weber (1968)
	16.27 ± 0.1	Higuchi et al. (1978)
	16.15 ± 0.06	Tamura et al. (1976)
	16.33 ± 0.1	Ghosh (1974)
20.5	16.08 ± 0.05	This study
	16.09 + 0.1	Stumm and Lee (1961)
10	15.86 ± 0.05	This study
	15.74 ± 0.05	Davison and Seed (1983)

a) The values of k are given for the NBS pH scale. Units of mol^{-3} kg H_2O^3 min^{-1}.

and

$$\ln K^*_W = 148.9802 - 13847.26/T - 23.6521 \ln T + 2[I^{1/2}/(1+1.2I^{1/2}) + 1.667 \ln(1+1.2I^{1/2})] \times (-5.8901 + 228.2338/T + 0.968144 \ln T) - I(20.6365 - 945.556/T - 3.00298 \ln T) - 0.18062[1 - (1 + 2I^{1/2} - 2I)\exp(-2I^{1/2})] - I^2(-0.05346 + 17.6216/T). \quad (33)$$

Equations (31), (32) and (33) should be valid over the pH, temperature and salinity range of most natural waters. We presently are in the process of making measurements in NaCl solutions to saturation. These studies will extend our present work to brines.

Comparisons with other studies

A comparison of our dilute solution (0.009 m $NaHCO_3$) results with literature data is shown in Table 8. It should be pointed out that these comparisons are made on the NBS scale ($[OH^-] = K_W/a_H$). The agreement is very good and demonstrates the reliability of our experimental techniques. Our extrapolated value of log k = 16.32 ± 0.05 is in good agreement with the value obtained by GHOSH (1974) for very dilute solutions of $NaHCO_3$ (0.001 M), but lower than the value of log k = 16.65 ± 0.2 obtained by SUNG and MORGAN (1980) in $NaClO_4$ solutions. DAVISON and SEED (1983) have made a comprehensive survey of the literature and selected a "universal" value of log k = 16.19 (with a range of 16.07 to 16.76). Our results are in excellent agreement with this value.

The reliability of these measurements for natural fresh waters deserves some comments. DAVISON and SEED (1983) concluded from their studies that the rate of oxidation of Fe(II) in lake waters was indistinguishable from their results in dilute $NaHCO_3$. At 10°C they found values of log k = 16.03 ± 0.14 and 16.11 ± 0.13, respectively, for oxic and anoxic lake waters. Both results are in good agreement with the value of log k = 16.10 ± 0.09 obtained by LAXEN and SHOLKOVITZ (1981) for anoxic lake waters. These natural water log k results are 0.17 to 0.25 higher than the value we found in 10°C. This difference, however, is almost within the experimental error of the measurements (0.2 in log k) and supports the contention of DAVISON and SEED (1983). It should be pointed out that at low levels of Fe(II) one might expect organic ligands to affect the rates. Unfortunately, it is not possible at present using spectroscopic methods to measure the rates of oxidation in natural waters at nanomolar levels of Fe (which may be the level for surface waters). We do feel that our low salinity results should be valid for fresh and estuarine waters with low levels of organic ligands.

It is difficult to make direct comparison of our seawater results with other studies due to the lack of details in the previous studies (see Table 9). The temperature of the measurements, for example, have not been reported in three of the previous studies. The most extensive measurements were made by ROEKENS and GRIEKEN (1983). Near a pH of 8.0 our results are in reasonable agreement at 15 and 25°C (see Table 9). Our half times (Eqn. 30) at a pH = 8 for S = 35 sea-

Table 9. Comparisons of the Half Times for the Oxidation of Fe(II) in Seawater Found by Various Workers.

pH	$t_{1/2}$	t°C	S	Media	Author
8.0	1.2 min.	25	35	Gulf Stream	This study[a]
	2.8	20			
	7.2	15			
8.15	2.7 (3.4)[a]	15	32	North Sea	Roekens & Grieken (1983)
8.44	1.3 (0.9)				
8.50	1.0 (0.7)				
7.72	3.0 (3.7)	25	32	North Sea	
8.0	3.3	?	36	Sargasso Sea	Kester et al. (1975)
	5.5	?	31.2	Narragansett Bay	
8.0	3.9	?	30	Puget Sound	Murray and Gill (1978)
8.2	3.7	?	35	Artificial Seawater	Waite and Morel (1984)

a) The values were determined from the overall equation (31).

water at 25°C ($t_{1/2}$ = 1.2 ± 0.3 min.) are faster than the values near 3 min. reported by KESTER *et al.* (1975), MURRAY and GILL (1978) and WAITE and MOREL (1984). If the measurements of these workers were made near room temperature (~20°C), the differences are not as great. One would not expect large differences due to the use of different pH scales. Studies with our electrode system (MILLERO, 1986) as well as others (BATES and MACASKILL, 1975) indicate the NBS and free pH scales are nearly equivalent. Another possible source of error in the literature results is problems of recording the actual pH of the measurements. If acidic stock solutions of Fe(II) were used, the actual pH of the measurements could be 0.1 units lower (SUNG and MORGAN, 1980) than the initial pH. This would cause the half times to be longer.

All of our seawater studies were made with Gulf Stream waters. These waters have low nutrients, organics and trace metals. One might expect the bay waters used in some of the previous studies to give longer half times due to the formation of iron organic complexes that have a slower rate of oxidation. The studies by KESTER *et al.* (see Table 9) support this contention.

To test this hypothesis and examine the reliability of our results for various seawaters we have made a number of measurements on Biscayne Bay waters. To be sure that our stock Fe(II) solutions did not influence our results we made a number of measurements in Gulf Stream seawaters. The results shown in Table 10 demonstrate that the rates are independent of the stock solution used. Since all of our measurements were made at high concentrations of Fe(II), we also examined the rates at various initial levels of iron. The results (see Table 11) at low levels of Fe(II) (less than 3 μM) have been made using the Ferrozine colorimetric technique (STOOKEY, 1970). As recently shown (LANDING, 1986) this method can be used in seawater to nanomolar levels of Fe(II). Measurements of the rate constant for the oxidation of Fe(II) in Gulf Stream and Biscayne Bay seawaters using the Ferrozine technique are given in Table 12. The results for the Gulf Stream and the incoming Bay waters give values for $t_{1/2}$ at a pH = 8.0 that are in reasonable agreement with those determined from Eqn. (30) (1.2 min). Measurements made at a lower pH (7.3 to 7.8) for the incoming waters were the same as those found for measurements made at the natural levels of pH (8.1 to 8.2). These results demonstrate that the second degree pH dependence apppears to hold for the Bay waters. The rates measured in the outflowing Bay waters showed large variations. The average half times were found to be 4.4 ± 1.0 min at pH = 8.0, the range being 2.4 to 6.2 min. These half times are 2 to 5 times longer than found for Gulf Stream waters. These differences are apparently due to the concentration of variable levels of organic ligands in the Bay waters. Measurements on ultrafiltered Bay waters supplied by Dr. Zika's group gave half times 2 times larger than Gulf Stream waters. Since the nominal molecular weight cutoff is ~500 (g mol^{-1}), these results indicate that lower molecular weight ligands are partly responsible for the effect. Since it is not possible at present to characterize these variable organic ligands, we are presently unable to give a more quantitative explanation. Rate measurements at low levels of Fe(II) for a number of different seawaters under controlled conditions are needed to clarify these effects. We feel, however, that our measurements should be valid for seawaters with low concentrations of organics and micromolar levels of Fe(II).

Table 11. The Rate Constant for the Oxidation of Fe(II) in Seawater at 25°C Obtained at Various Levels of Initial Fe(II).

$[Fe(II)]^0$	log k^a
50 μM	14.61
40	14.66
30	14.61
20	14.56
10	14.59
3	14.60
	14.61 ± 0.04
Overall Equation	14.68 ± 0.09

a) For S = 35 seawater and t = 25°C

Table 10. Comparisons of the Rates of Fe(II) Oxidation in Seawater Obtained by Using Various Stock Solutions.

Stock Solution	log k^a	$t_{1/2}$ (pH = 8)
$FeCl_2$	14.63 ± 0.03	1.2 min
$FeSO_4$	14.59 ± 0.06	1.3
$Fe(NH_4)_2(SO_4)_2$	14.64 ± 0.05	1.2
Fe(electrolytic)	14.57 ± 0.02	[illegible]
Average	14.62 ± 0.03	1.3 ± 0.1
Overall Equation	14.68 ± 0.09	1.2 ± 0.3

a) For S = 35 seawater, t = 25°C, and $[Fe(II)]^0$ = 50 μM

Table 12. Measurements of the Rates of Oxidation of Fe(II) in Various Ocean Waters at 25°C.

pH Range	log k^a	$t_{1/2}$ (pH = 8.0)	water
[illegible] to 8.2	14.59 ± 0.06 (10)	1.5 ± 0.2 min	Gulf Stream
8.1 to 8.2	14.50 ± 0.06 (17)	1.6 ± 0.2	Biscayne Bay
7.3 to 7.8	14.53 ± 0.07 (10)	1.7 ± 0.2	(incoming tide)
8.1 to 8.3	14.13 ± 0.09 (20)	4.4 ± 1.0	Biscayne Bay (outgoing tide)
8.13 to 8.19	14.39 ± 0.04 (7)	[illegible]	Biscayne Bay^b (ultrafiltered)

a) Made using the Ferrozine technique (Stookey, 1970) at an initial concentration of iron of 3 μM. The salinities were all near S = 35.0. The numbers in parentheses give the number of runs made.

b) Ultrafiltered Bay water (Nuclepore 500 Dalton [illegible]) supplied by P. Milne and R. Zika.

CONCLUSIONS

The kinetics of oxidation of Fe(II) have been studied as a function of pH, temperature, and salinity for Gulf Stream seawaters. The overall rate constants (k)

$$-d[\mathrm{Fe(II)}]/dt = k[\mathrm{Fe(II)}][\mathrm{O_2}][\mathrm{OH^-}]^2$$

have been fit to the equation

$$\log k = 21.56 - 1545/T - 3.29I^{1/2} + 1.52I.$$

The rate constants for fresh waters and seawaters were found to be in reasonable agreement with literature data. Measurements on Biscayne Bay waters indicate that variable levels of dissolved organics can increase the life times when compared to open ocean waters. Further measurements are needed to elucidate these effects and examine their significance on the mechanism of the oxidation.

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