

Oxidation kinetics of Fe^{2+} in aqueous solutions

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1 Aims and objectives

In this practical, you will:

1. Investigate the kinetics of the Fe^{2+} to Fe^{3+} oxidation in natural waters
2. Analyse a rate law of second order
3. Determine the rate law of the Fe^{2+} oxidation reaction
4. Apply UV-Vis spectroscopy as an analytical method, using external calibration

2 Introduction

2.1 Iron in aqueous solutions

Iron can exist in aquatic systems (natural waters, sediments, algae) in several oxidation states: metallic iron (iron metal), ferrous iron (Fe^{2+}), and ferric iron (Fe^{3+}). The oxidation state in which iron exists in a particular aquatic system, and the redox reactions (chemical oxidation-reduction reactions) in which it participates, depend on the presence or absence of dissolved oxygen.

The sediments of many, if not most, aquatic systems are anoxic (without oxygen) as a result of the bacterial oxidation of particulate organic matter. Sediment organic matter includes dead and decomposing aquatic plants, algae and other organisms that settle to and become part of the sediments. In some waters, anthropogenic oxygen-demanding material (particulate biochemical oxygen demand, such as from wastewater treatment plant effluents) also accumulates in sediments. In such an anoxic environment, iron exists in the sediment in the reduced form, ferrous iron (Fe^{2+}). In that form, it is often associated with sulphide, as black, iron sulphide.

In the oxic (oxygen-containing) water column, iron is in the oxidized, ferric form (Fe^{3+}), existing as particulate or colloidal ferric hydroxide (hydrrous oxide). This form of iron is a scavenger

of many types of chemicals including some heavy metals, organics, and phosphorus. Association with ferric hydroxide affects the bioavailability of these chemicals; associated with ferric hydroxide, they are largely unavailable or non-toxic to organisms.

2.2 Theory of Fe²⁺ oxidation

For the oxidation of Fe²⁺ to Fe³⁺, the following rate law has been proposed [Emmenegger et al., 1998; Stumm and Morgan, 1996]:

$$r = -d[\text{Fe}^{2+}] / dt = k [\text{Fe}^{2+}] [\text{OH}^-]^2 p_{\text{O}_2} \quad (1)$$

If this holds, then we can formulate the following two hypotheses:

- i.) The reaction rate depends linearly from the [Fe²⁺] and the p_{O2}; and
- ii.) The reaction rate depends quadratically on the [OH⁻] concentration.

We can test these two hypotheses using a simple experimental set up where Fe²⁺ solutions at different pH values and known [Fe²⁺] concentrations are purged with air (or oxygen) and sub samples are collected at different time intervals.

To test the first hypothesis, we need to keep [OH⁻] and p_{O2} constant. The above rate law (1) is then reduced to a reaction of pseudo first order (2):

$$r = -d[\text{Fe}^{2+}] / dt = k_1 [\text{Fe}^{2+}] \quad (2)$$

, where $k_1 = k p_{\text{O}_2} [\text{OH}^-]^2$. Reactions of first order give a linear relationship in a ln[Fe²⁺] vs. time plot.

To test the second hypothesis, we need to do several oxidation experiments. The rate constant k_1 is determined at different partial pressures of oxygen and at different pH values. Using the log of equation 1, we get:

$$\log k_1 = \log k + \log p_{\text{O}_2} + 2 \log [\text{OH}^-] \quad (3)$$

If the second hypothesis is correct, then a plot of log k_1 vs. pH should have a slope of +2 and the values for k_1 for air and oxygen should differ from a factor of 5.

3 Experimental procedure

3.1 Preparation of solutions (each group)

1. Prepare 50 ml 1 M imidazole buffer (adjusting to pH 6.0 with concentrated H₂SO₄);
2. Prepare 50 ml 0.5 M NaOH solution;
3. Prepare 50 ml 0.1 M H₂SO₄ solution (USE FUME HOOD UNDER SUPERVISION OF THE DEMONSTRATOR);
4. Prepare 2.6 M acetate buffer using 24 ml acetic acid, 100 g NH₄-acetate and 500 ml distilled deionized (DD) water;
5. Prepare 250 ml 0.02 M Fe²⁺ solution using 247.5 ml DD water, 2.5 ml 0.1 M H₂SO₄, and 1.70 g Fe(NH₄)₂(SO₄)₂•6H₂O;
6. Prepare 100 ml 0.03 M ferrozine solution using 1.63 g ferrozine and 100 ml DD water;
7. Prepare six Fe²⁺ standard solutions (0 - 50 μM) as the calibration curve (see the Table 1 in annexes for details);

8. The calibration standards, imidazole buffer, H_2SO_4 and acetate buffer might be prepared by the instructor in advance given for the limited time.

3.2 Buffer systems

During the oxidation tests, the solution pH is kept constant at a targeted level by adding the imidazole buffer, which does not complex with Fe^{2+} and thus doesn't influence the oxidation reaction.

3.3 Determination of Fe^{2+}

The Fe^{2+} concentration is determined based on the formation of a colourful Fe^{2+} -ferrozine complex. The colour intensity of the Fe-ferrozine complex is directly proportional to the concentration of Fe^{2+} , and the maximal absorption of the complex is at $\lambda = 562 \text{ nm}$.

3.4 Experimental procedure (each student)

1. Prepare 18 test tubes (e.g., 15 ml centrifuge tubes) for six time-point sampling * three replicates. Add 1 ml of the acetate buffer and 0.1 ml of the ferrozine solution, and slightly shake to mix the solution.
2. Add 0.5 ml of the 1 M imidazole buffer into 100 ml of the bottled water, and slightly shake to mix the solution.
3. The solution pH is adjusted to the targeted level by adding NaOH/acid (a pH-electrode is required), and the solution is purged with air or oxygen.
4. Start the oxidation by adding 0.2 ml of the 0.02 M Fe^{2+} solution, and run the timer.
5. Take 5 ml samples into each of the prepared test tubes as soon as possible, note the running time, and slightly shake to mix the solution.
6. Take other samples according to a selected time interval, and note the running time. Six time points in total in our case.
7. Measure the samples and the calibration standards with an ultraviolet–visible spectrophotometer at $\lambda = 562 \text{ nm}$.
8. After the experiment, all glassware/tubes are cleaned with the 0.1 M H_2SO_4 solution to remove any adsorbed Fe^{3+} -hydroxide, and then rinsed three times with DD water.

Note, in practice the oxidation test should be done between 7.2 and 7.9, otherwise the reaction would be too slow or too fast to be measured.

3.5 Data analysis

1. Calculate the $[\text{Fe}^{2+}]$ in your samples by using the calibration curve and by taking into account the dilutions made,
2. Make a plot of $\ln [\text{Fe}^{2+}]$ vs. t for the different pH experiments and determine the apparent rate constants (k_1),
3. Make a plot of $\log k_1$ vs. pH and determine the slope,
4. Make a qualitative error estimate.

4 Questions

1. What is the dependence between reaction speed and pO_2 ?
2. What effects of changing $[OH^-]$ have you observed?
3. Where is the error?
4. Do we have in natural waters a lot or little Fe^{2+} ? What is the significance of this?
5. Read carefully the attached paper [Emmenegger *et al.*, 1998]. Compare your rates with the ones determined in the lake. Do you observe the same effect of changing pH?

5 Literature

Atkins, P.; Paula, J. De. *Atkins' physical chemistry*; 2009.

Emmenegger, L., et al. (1998), *Oxidation kinetics of $Fe(2+)$ in a eutrophic Swiss lake*, Environ. Sci. Technol., 32, 2990-2996.

Harris, D. C., (2010), *Quantitative chemical analysis*, Eighth Edition, 719 pp, Freeman Palgrave Macmillan.

Stumm, W.; Lee, G. F. *Ind. Eng. Chem.* **1961**, 53 (2), 143–146.

Stumm, W., and Morgan, J.J., (1996), *Aquatic Chemistry*, Third Edition ed., 1017 pp., John Wiley and Sons.

6 Annexes

6.1 Paper [Emmenegger *et al.*, 1998]

6.2 Derivation of the Fe^{2+} oxidation rate law

Reactions rates follow the form

$$v = k_r [A]^a [B]^b [C]^c \dots \text{etc}$$

where v is the rate of reaction, k_r is the rate constant, $[A]$, $[B]$ and $[C]$ are the concentrations of each species, and a , b and c is the order of the reaction with respect to the respective species ¹. Students were reminded that the order of reaction for any given species is not necessarily equivalent to its stoichiometry in the given reaction, and instead must be determined experimentally. There are two popularly used methods for determining the order of a reaction for any given reactant species. Perhaps the best known is the method of initial rates, where the order of reaction for given species A is determined from the first derivative (gradient) of the plot of $[A]$ versus time at $t=0$. A second method, used in this study, is the integrated rate law method. For a first order reaction, the rate of decrease in concentration of a reactant is proportional to the concentration of the species remaining

$$d[A]/dt = -k_r [A] \quad dt$$

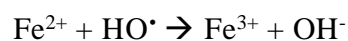
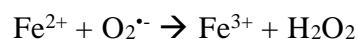
The integration of this expression gives

$$\int [A]_0 \rightarrow [A] \, d[A]/[A] = -k_r \int 0 \rightarrow t \, dt$$

$$\ln([A]/[A]_0) = -k_r t$$

Indicating that for a first-order reaction, a plot of $\ln([A]/[A]_0)$ vs t , a straight line should be found, with a slope of $-k$ (Atkins and Paula 2009)

Stumm and Lee (1961) showed that the rate law for Fe^{2+} oxidation is first order with respect to both $[\text{Fe}^{2+}]$ and the partial pressure of oxygen, and second order with respect to the concentration of hydroxide ions, $[\text{OH}^-]^2$. For naturally occurring water systems, the reactions of relevance are



(Emmenegger *et al.* 1998)

Giving the combined rate equation of $v = k[\text{Fe}^{2+}][\text{O}_2][\text{OH}^-]^2$. Previous cohorts in this lab course have investigated the effects of oxygen partial pressure on the rate of reaction by measuring the effects of bubbling oxygen or nitrogen gas through the solution. However this cohort considered the rate dependence on hydroxide concentration (measured through pH) as well as $[\text{Fe}^{2+}]$.

6.3 Student data sets

Table 1. Calibration method which keeps [acetate] and [ferrozine] constant

Stand-ard	[Fe] μM	Comment	Vol Fe to add (ml)	Vol Ferrozine carried over (ml)	Vol ferrozine to add to standard (ml)	Vol acetate carried over (ml)	Vol acetate to add to standard (ml)	Vol DD water (ml)	Total vol (ml)
Initial [Fe]	20,000								
Stock solution	500		0.25					9.75	10
S6	50	Dilution from stock for standards	0.61	0	0.1	0	1	4.39	6.1
S5	25	Dilution from S6	3.05	0.05	0.05	0.5	0.5	2.50	6.1
S4	5	Dilution from S5	1.22	0.02	0.08	0.2	0.8	4.00	6.1
S3	1	Dilution from S4	1.22	0.02	0.08	0.2	0.8	4.00	6.1
S2	0.5	Dilution from S3	3.05	0.05	0.05	0.5	0.5	2.50	6.1
S1	0	Blank	0	0	1	0	0.1	5	6.1

Table 2. Calibration data for Fe²⁺ concentration determined by UV/Vis spectroscopy.

Group 1		Group 2		Group 3		Group 4	
[Fe ²⁺] μM	Absorbance	[Fe ²⁺] μM	Absorbance	[Fe ²⁺] μM	Absorbance	[Fe ²⁺] μM	Absorbance
0	0	0	0	0	0	0	0
0.5	0.021	0.5	0.006	0.5	0.014	0.4	0.015
1	0.028	1	0.023	1	0.039	1	0.024
5	0.139	5	0.124	5	0.132	4	0.085
25	0.696	25	0.635	25	0.69	20	0.491
50	1.372	50	1.259	50	1.391	40	1

Table 3. Student's kinetic experiment results with DI Water*Group 1*

pH (start):	7.23	pH (end):	7.20	pH (start):	7.79	pH (end):	7.69
		[Fe(II)]				[Fe(II)]	
t (s)	Abs	(μM)	$\ln[\text{Fe(II)}]$	t (s)	Abs	(μM)	$\ln[\text{Fe(II)}]$
0	1.000	36.4	3.59	5	0.903	32.8	3.49
127	0.879	32.0	3.46	30	0.766	27.8	3.33
420	0.815	29.6	3.39	70	0.658	23.9	3.17
700	0.735	26.7	3.28	102	0.538	19.5	2.97
947	0.607	22.0	3.09	136	0.393	14.2	2.65
1244	0.449	16.3	2.79	175	0.258	9.3	2.23
1872	0.191	6.9	1.92	211	0.163	5.8	1.76
				246	0.107	3.8	1.33
				286	0.071	2.5	0.90
				324	0.039	1.3	0.26

Group 2

pH (start):	7.48	pH (end):	7.45	pH (start):	7.61	pH (end):	7.60
		[Fe(II)]				[Fe(II)]	
t (s)	Abs	(μM)	$\ln[\text{Fe(II)}]$	t (s)	Abs	(μM)	$\ln[\text{Fe(II)}]$
10	0.762	30.2	3.41	14	0.865	34.3	3.53
90	0.756	30.0	3.40	42	0.779	30.9	3.43
187	0.591	23.4	3.15	140	0.579	23.0	3.13
310	0.447	17.8	2.88	235	0.355	14.1	2.65
430	0.231	9.2	2.22	310	0.249	9.9	2.30
492	0.179	7.2	1.97	340	0.171	6.8	1.92
566	0.121	4.9	1.58	407	0.165	6.6	1.89
640	0.077	3.1	1.14	435	0.110	4.4	1.49
735	0.040	1.7	0.51	505	0.067	2.7	1.00
795	0.042	1.7	0.56	535	0.037	1.5	0.44

Table 3. Student's kinetic experiment results with DI Water*Group 3*

pH (start):	7.59	pH (end):	7.54	pH (start):	7.41	pH (end):	7.40
t (s)	Abs	[Fe(II)] (μM)	ln[Fe(II)]	t (s)	Abs	[Fe(II)] (μM)	ln[Fe(II)]
10	0.898	35.6	3.57	7	0.756	30.0	3.40
39	0.815	32.3	3.47	66	0.820	32.5	3.48
95	0.697	27.6	3.32	127	0.720	28.5	3.35
150	0.545	21.6	3.07	246	0.623	24.7	3.21
185	0.477	18.9	2.94	306	0.425	16.9	2.83
214	0.395	15.7	2.75	366	0.342	13.6	2.61
242	0.328	13.0	2.57	424	0.271	10.8	2.38
278	0.266	10.6	2.36	485	0.208	8.3	2.12
331	0.175	7.0	1.95	526	0.167	6.7	1.90
379	0.123	4.9	1.60	607	0.138	5.5	1.71

Table 3. Student's kinetic experiment results with DI Water*Group 4*

pH (start):	7.25	pH (end):	7.21	pH (start):	7.80	pH (end):	7.74	pH (start):	7.47	pH (end):	7.45
t (s)	Abs	[Fe(II)] (μM)	ln[Fe(II)]	t (s)	Abs	[Fe(II)] (μM)	ln[Fe(II)]	t (s)	Abs	[Fe(II)] (μM)	ln[Fe(II)]
13	0.898	33.7	3.52	7	0.858	32.2	3.47	7	0.902	33.8	3.52
178	0.824	30.9	3.43	38	0.766	28.7	3.36	35	0.874	32.8	3.49
360	0.766	28.7	3.36	64	0.645	24.1	3.18	92	0.771	28.9	3.36
542	0.679	25.4	3.24	97	0.501	18.7	2.93	208	0.574	21.5	3.07
720	0.615	23.0	3.14	125	0.352	13.1	2.57	333	0.361	13.5	2.60
903	0.520	19.4	2.97	164	0.217	8.0	2.08	444	0.217	8.0	2.08
1083	0.442	16.5	2.80	192	0.138	5.1	1.62	564	0.120	4.4	1.48
1255	0.360	13.4	2.60	222	0.087	3.1	1.15	690	0.088	3.2	1.16
1440	0.295	11.0	2.40	270	0.038	1.3	0.26	807	0.042	1.5	0.37
1622	0.237	8.8	2.17	301	0.027	0.9	-0.12	923	0.015	0.4	-0.83

Table 4. Conditional rate constant (k') data collected from the slope of the iron oxidation experiments.

pH	pOH	k' (s^{-1})	$\log(k')$
7.23	6.77	$8.31 \pm 0.51 \times 10^{-4}$	-3.08 ± 0.03
7.23 (2)	6.77	$8.35 \pm 1.08 \times 10^{-4}$	-3.08 ± 0.06
7.41	6.59	$3.15 \pm 0.26 \times 10^{-3}$	-2.50 ± 0.04
7.45	6.55	$4.39 \pm 0.31 \times 10^{-3}$	-2.36 ± 0.03
7.45 (2)	6.55	$4.06 \pm 0.28 \times 10^{-3}$	-2.39 ± 0.03
7.55	6.45	$5.29 \pm 0.34 \times 10^{-3}$	-2.28 ± 0.03
7.61	6.39	$5.47 \pm 0.41 \times 10^{-3}$	-2.26 ± 0.03
7.70	6.30	$1.01 \pm 0.06 \times 10^{-2}$	-2.00 ± 0.03
7.76	6.24	$1.28 \pm 0.08 \times 10^{-2}$	-1.89 ± 0.03