

Kinetics, geochemical modeling

1) Half lives

The reaction $2A + B \rightarrow C + D$ goes to completion and follows the following rate law:

$$-d[A]/dt = k[A]^2[B] = -2 d[B]/dt$$

a) Calculate the missing half live for the following system. Explain your answer.

A_0 (μM)	B_0 (μM)	$t_{1/2}$ (s)
300	4	62.2
400	5	

b) Calculate the missing half live for the following system. Explain your answer.

A_0 (μM)	B_0 (μM)	$t_{1/2}$ (s)
5	300	625
10	300	

2) Rate constant for Fe^{II} oxidation

Over a wide range of pH (~ 5 – 9), oxidation of Fe^{II} by O_2 is described by the rate equation $-d[\text{Fe}^{\text{II}}]/dt = k[\text{Fe}^{\text{II}}]P_{\text{O}_2}[\text{OH}^-]^2$. The rate thus is highly pH dependent. If rate measurements are made in buffered solutions at fixed pH and if the partial pressure of oxygen is held constant (e.g., by sparging the solution with a gas having a fixed P_{O_2}), the reaction becomes pseudo-first order ($-d[\text{Fe}^{\text{II}}]/dt = k_{\text{obs}}[\text{Fe}^{\text{II}}]$).

The following data on $[\text{Fe}^{\text{II}}]$ were obtained using the phenanthroline colorimetric method in solutions with an ionic strength of 0.0010 buffered to pH 7.00 with P_{O_2} held at 0.21 atm by sparging with clean air. Compute

a) k' , the observed pseudo-first-order rate constant for the reaction

b) the half-life of Fe^{II} under the reaction conditions

c) k , the rate constant for the complete rate reaction (in $\text{M}^{-2} \text{atm}^{-1} \text{min}^{-1}$). Use an activity coefficient γ for OH^- of 0.965 at $I = 0.001$ and the relationship $\{\text{OH}^-\} = \gamma_i * [\text{OH}^-]$.

Time (min)	0	10	20	30	40	60
$[\text{Fe}^{\text{II}}]$ ($\mu\text{g L}^{-1}$)	500	320	200	130	80	35

3) Acetoclastic methanogenesis

Methanogenesis is carried out by strictly anaerobic bacteria under the most extreme reduced conditions. There are three pathways for methanogenesis, one of which, acetoclastic methanogenesis, uses acetate. Consider a freshwater sediment at 25°C with 10^{-6} M acetate, 10^{-3} M HCO_3^- , and 10^{-6} M dissolved methane. Use Rxn in the Geochemist's Workbench to answer the following questions:

- a) What is the overall chemical reaction?
- b) Is this a redox reaction? If so, does acetate serve as the electron donor or electron acceptor?
- c) What is the log K and Gibbs free energy of the reaction? Do you expect the reaction to occur spontaneously under the given conditions?

4) pe-pH diagram for As

In Homework 4 (exercise 4) you manually constructed the pe-pH diagram for As. Now, use Act2 in the Geochemist's workbench to create an As pe-pH diagram. Which differences, if any, do you observe and why?