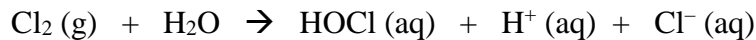


Fate & Transport of Chemicals in the Environment

Homework #6
Due Wednesday, March 2, 2022

University of South Florida
Prof J A Cunningham

1. In environmental engineering, we use chlorine to disinfect water. Chlorine can be added in a gaseous form, as Cl_2 (g), or in a liquid form, as an aqueous solution of NaOCl. For this problem, let's suppose we are using the gaseous form. When chlorine gas is added to water, the following irreversible reaction takes place (hydrolysis of Cl_2):



One of the species formed by the hydrolysis of gaseous chlorine is hypochlorous acid, HOCl. Hypochlorous acid dissociates to form hypochlorite in the following reversible equilibrium.



...and of course, the H^+ ion is in equilibrium with the OH^- ion.



For now, let's suppose that we added chlorine gas to perfectly pure H_2O which is initially at $\text{pH} = 7$. Pure water doesn't actually exist in nature, but for now let's suppose it did. Let's suppose we dose the chlorine into the water at a concentration of 7.1 mg/L, i.e., 7.1 mg of Cl_2 (g) per liter of water. That is a pretty realistic dose for disinfection purposes.

- Estimate/calculate the chlorine dose in units of mol/L.
- Assume that the hydrolysis of Cl_2 (g) proceeds to completion rapidly. Estimate/calculate the molar concentration of Cl^- (aq) produced. Hint: it's easy; don't make it difficult.

You just found the concentration of Cl^- (aq) that will result when we add 7.1 mg/L of chlorine gas to the pure water. We also want to know the concentrations of the other species in the water: H^+ (aq), OH^- (aq), HOCl (aq), and OCl^- (aq). That is four unknowns. So we need four equations. We have two of the four necessary equations – the two equilibria that I wrote above, with their equilibrium constants given. We need two more equations. These two equations are a mass balance equation and a charge balance equation.

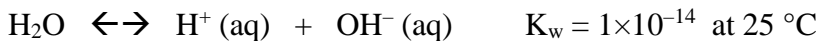
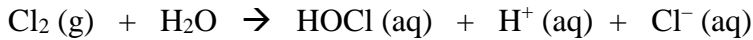
Mass balance: $[\text{HOCl}] + [\text{OCl}^-] = \text{total molar concentration of } \text{Cl}_2 \text{ added (from part a)}$

Charge balance: $[\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-] + [\text{OCl}^-]$

- Estimate/calculate the concentrations of H^+ (aq), OH^- (aq), HOCl (aq), and OCl^- (aq). Hint: identify which term on the right-hand side of the charge balance will be the dominant term. Then you can rapidly solve for $[\text{H}^+]$, and then the rest of it is pretty easy.
- Estimate/calculate the pH. Does Cl_2 gas act like an acid or a base? Explain briefly.

2. Let's continue thinking about chlorination of water, but now let's take into account the fact that pure water doesn't actually exist in nature. Suppose we add our chlorine gas to water that contains 0.005 M of sodium bicarbonate, NaHCO_3 . (That might be a decent estimate for spring-fed river water.) The water is at $\text{pH} = 9$ before chlorination. We'll add our chlorine gas at a concentration of 7.1 mg/L, just like we did in problem 1. Again we want to calculate the concentrations of all the species in the water, and also the pH.

The first four equations from problem (1) are still valid:



Hypochlorite mass balance: $[\text{HOCl}] + [\text{OCl}^-] = \text{total molar concentration of } \text{Cl}_2 \text{ added}$

However, now we have some additional chemical species in the system. In addition to the five species we had in problem 1 (Cl^- , H^+ , OH^- , OCl^- , and HOCl), we now have an additional three species. They are $\text{Na}^+(\text{aq})$, $\text{H}_2\text{CO}_3(\text{aq})$, and $\text{HCO}_3^-(\text{aq})$. That makes 8 species altogether. We need 8 equations! There are four up above. We need four more. Here they are.



$$[\text{Na}^+] = 0.005 \text{ M}$$

Carbonate mass balance: $[\text{H}_2\text{CO}_3(\text{aq})] + [\text{HCO}_3^-] = 0.005 \text{ M}$

Updated charge balance: $[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-] + [\text{OCl}^-] + [\text{HCO}_3^-]$

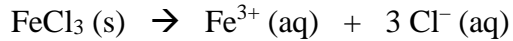
- Estimate/calculate the concentrations of all 8 species in the water. Eight equations for 8 unknowns!
- Estimate/calculate the pH. How does the pH in problem 2 compare to the pH in problem 1? How does the pH *change* in problem 2 compare to the pH *change* in problem 1? What can you conclude about the effect of having bicarbonate in the water? We often say that bicarbonate *provides alkalinity* or that bicarbonate *buffers* the water.

This problem can get pretty messy if we're not clever about it. However, we know $[\text{Cl}^-]$ and $[\text{Na}^+]$ right away, so that is two down; only six to go! The key trick is identifying which terms in the charge balance are significant and which ones can be treated as sufficiently small to ignore in the charge balance. In this problem, the charge balance can be approximated as the following:

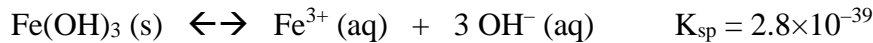
$$[\text{Na}^+] \approx [\text{Cl}^-] + [\text{HCO}_3^-]$$

So you can get a decent estimate at $[\text{HCO}_3^-]$. Then it's off to the races.

3. Another chemical we use when we treat water is ferric chloride, FeCl_3 . This is a popular coagulant. When we add ferric chloride to water, it dissolves almost completely, so we treat it as an irreversible (one-way) reaction instead of a reversible equilibrium.



The ferric iron then reacts with hydroxyl ions in the water to precipitate as $\text{Fe}(\text{OH})_3$. The precipitation/dissolution equilibrium for this is



Suppose we add ferric chloride to pure water at a dose of 16.2 mg/L. This is another example where we are over-simplifying by assuming that the water is pure, but it's OK for the purposes of this exercise.

- a. Estimate/calculate the molar concentration of $\text{Cl}^- (\text{aq})$ that will result.

Now we want to estimate the concentrations of all the other aqueous species present: $\text{Fe}^{3+} (\text{aq})$, $\text{H}^+ (\text{aq})$, and $\text{OH}^- (\text{aq})$. That means we need three equations. One of them is the precipitation/dissolution equilibrium given above. One of them is the equilibrium between H^+ and OH^- . The final equation is a charge balance.

$$3 [\text{Fe}^{3+} (\text{aq})] + [\text{H}^+ (\text{aq})] = [\text{Cl}^- (\text{aq})] + [\text{OH}^- (\text{aq})]$$

- b. Estimate/calculate the molar concentrations of $\text{Fe}^{3+} (\text{aq})$, $\text{H}^+ (\text{aq})$, and $\text{OH}^- (\text{aq})$. There are different ways that you could go about solving the three equations in the three unknowns. A spreadsheet can help if you want to solve by trial-and-error.
- c. Estimate/calculate the pH. Does FeCl_3 act as an acid or as a base when added to water?

The dose of 16.2 mg/L might be pretty realistic. However, the final pH that we found is not very realistic, because we don't add FeCl_3 to pure water. To get a more realistic estimate of the pH, we would need to account for the presence of other chemical species, like bicarbonate. We won't worry about that for now.

4. Years ago, I was part of a research project in which the team added nitrate and sulfate to groundwater in order to stimulate bacteria to degrade petroleum hydrocarbons after a gasoline spill. You can read about the project in these two papers:

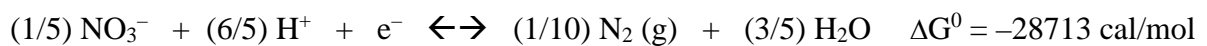
Cunningham JA, Rahme H, Hopkins GD, Lebrón CA, Reinhard M. **2001**. Enhanced *in situ* bioremediation of BTEX-contaminated groundwater by combined injection of nitrate and sulfate. *Environmental Science & Technology*, 35(8), 1663–1670.

Cunningham JA, Hopkins GD, Lebrón CA, Reinhard M. **2000**. Enhanced anaerobic bioremediation of groundwater contaminated by fuel hydrocarbons at Seal Beach, California. *Biodegradation*, 11(2-3), 159–170.

One interesting thing that we observed was that when we added nitrate to the groundwater, we saw a big spike of sulfate show up. That was a bit of a surprise. We hypothesized that there had been bisulfide (HS^-) in the water, and then the bisulfide was oxidized to sulfate when the nitrate was added. We can use Table 2.5 in your text book to see if this is a good hypothesis.

- Combine the fourth and fifth equations in the table to create a new half-reaction in which sulfate (SO_4^{2-}) accepts an electron to form hydrogen sulfide (H_2S). You'll need to think about how to combine the two equations properly. Your new half-reaction should be written so that the stoichiometric coefficient on the electron is 1.
- Estimate/calculate ΔG^0 and $\log_{10}(K_{\text{eq}})$ for your new half-reaction.

Your book doesn't include a half-reaction for the conversion of nitrate (NO_3^-) to nitrogen gas (N_2). It has half-reactions for nitrate reduction to nitrite (NO_2^-) and for nitrate reduction to ammonium (NH_4^+), but not for reduction to N_2 . Here it is:

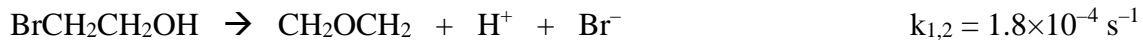


- Combine your half-reaction from part (a) with this half-reaction for nitrate reduction to N_2 gas. Write the expression for the reaction of NO_3^- with H_2S to form SO_4^{2-} and N_2 gas.
- Estimate/calculate ΔG^0 and $\log_{10}(K_{\text{eq}})$ for your reaction in part (c). Based on your ΔG^0 and K_{eq} , does the reaction proceed in the forward direction? Based on that, does it look like our hypothesis about sulfate formation from NO_3^- and HS^- was reasonable?

NOTE: Your text book gives ΔG^0 values, which means the free-energy change of the reaction *at standard state / standard conditions*. One of these conditions is that the $\text{pH} = 0$, which is not realistic for environmental conditions. Some text books use a different framework called $\Delta G^{0'}$, which is based on $\text{pH} = 7$ rather than $\text{pH} = 0$. That is a better framework for environmental systems, and it would actually give us a better indication whether the reaction proceeds. But we will work with ΔG^0 because that is what your book uses. It is good enough for this problem.

5. The chemical 1,2-dibromoethane is commonly (and mistakenly) called “ethylene dibromide,” or EDB. EDB was banned in the 1980s, but it still shows up sometimes at contaminated sites. The good news is that EDB does undergo different types of degradation reactions, like photolysis and biodegradation.

In shallow surface water, photolysis might be important. Castro and Belser (1985) wrote that the following photolysis reactions occur in water, with apparent first-order kinetics.



- Look at the reaction of EDB with water, i.e., the first reaction written above. Why is it OK to treat this as a first-order reaction even though it is the reaction of EDB with water? Why don't we need to treat it as second-order?
- What half-life would we expect for EDB based on the reactions above?

Notice that the reactions above are sequential first-order reactions. Also, the last reaction (hydrolysis of epoxide) is slow, with a half-life of 10 d, so let's temporarily ignore that reaction because it is so slow. In that case, the three reactions above follow a pattern that looks like



where A means EDB, B means bromoethanol, and C means epoxide.

For a system like this in a well-mixed batch reactor, we would have the following differential equations:

$$d[A]/dt = -k_{1,1} [A]$$

$$d[B]/dt = k_{1,1} [A] - k_{1,2} [B]$$

$$d[C]/dt = k_{1,2} [B]$$

subject to some initial concentrations $[A]_0$, $[B]_0$, and $[C]_0$.

- Suppose we can consider a shallow pond as a well-mixed batch system. Initially, at time $t = 0$, the concentration of EDB in the pond is $1 \mu\text{M}$, but there is no bromoethanol or epoxide in the water. Graph the concentrations of EDB, bromoethanol, and epoxide as functions of time over a period of 8 hr. (It should be OK to ignore the third reaction during the first 8 hr because the half-life is much longer than that.) This will require you to solve the differential equations – or to look up the solution for sequential first-order reactions. Try to solve the equations, but if you can't do it, look up the answer somewhere.

6. In anaerobic groundwater, the photolysis of EDB will not occur because groundwater is not exposed to light. However, the news is not all bad. Yu et al. (2013, DOI 10.1128/AEM.02163-12) reported that EDB can be biodegraded under anaerobic conditions. The kinetics of the biodegradation follow Monod kinetics. The value of μ_{\max} is approximately 0.3 d^{-1} and the value of K_S is approximately $15 \text{ }\mu\text{M}$. I don't think the yield coefficient was reported, but let's assume it is 0.5 mg/mg – that probably won't be too far off.
- a. Let's assume that the concentration of EDB in the groundwater is $1 \text{ }\mu\text{M}$, as we did in problem #5. Also, let's temporarily assume that the concentration of bacteria is 1 mg/L . Under those conditions, what is the rate of EDB degradation, according to the Monod kinetic expression? What if we approximate the reaction as first-order by assuming $[\text{EDB}] \ll K_S$? – under this assumption, what rate would you estimate? Is this approximation OK? i.e., does the approximate rate using the first-order expression come out pretty close to the rate you'd get using the full Monod expression?
 - b. Estimate/calculate the half-life of EDB you'd expect in anaerobic groundwater, based on the assumed bacterial concentration of 1 mg/L that we used in part (a). Hint: to make this calculation, you will need to convert K_S to units of mg/L instead of μM .
 - c. What concentration of bacteria would you need to have in the groundwater in order to achieve a half-life equal to that from problem 5(b)? Does this look like a realistic bacterial concentration for groundwater? Based on that, in what environment would EDB persist longer – in shallow surface water, or in anaerobic groundwater?