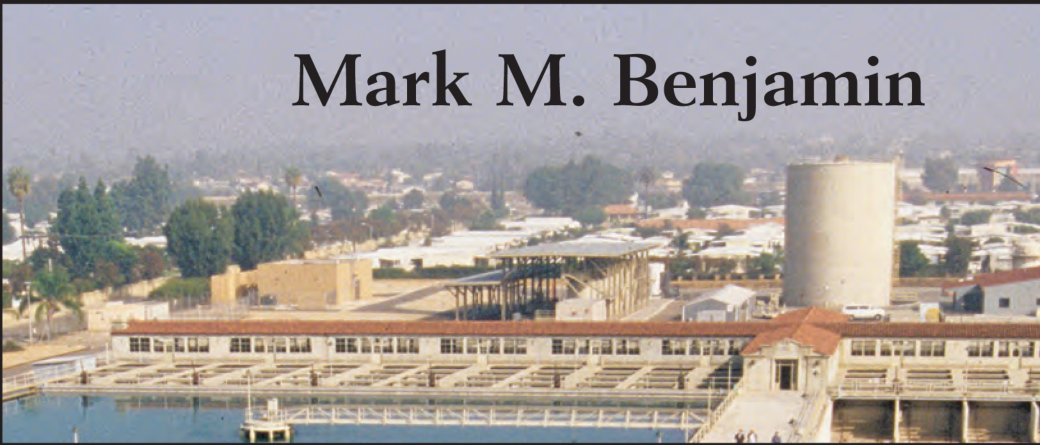
Second Edition

Water Chemistry



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Complete
Revised

Homework Problems

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CHAPTER 1 HOMEWORK PROBLEMS

1. An aqueous solution is prepared by adding 110 mg of calcium chloride ($CaCl_2$) and 50 mg of calcium sulfate ($CaSO_4$) to 500 mL of water. The solution pH is 8.0 $\left([\mathrm{H}^+] = 10^{-8}\,M, [\mathrm{OH}^-] = 10^{-6}\,M\right)$.

    (a) Assuming that the salts dissociate completely, express the concentration of each of the dissociation products (Ca^{2+}, Cl^-, and SO_4^{2-}) in mg/L, millimolar, and normal (*N*) units.

    (b) If the total molar concentration of all species in the solution is the same as in pure water, what are the mole fractions of H^+, OH^-, Ca^{2+}, Cl^-, and SO_4^{2-}, and H_2O?

2. A solution contains 45 mg/L Ba^{2+}. A consultant has suggested that the Ba^{2+} could be removed from solution by converting it to solid barium sulfate [$BaSO_4(s)$]. To accomplish this, she proposes adding enough Na_2SO_4 to the solution to convert all the Ba^{2+} to $BaSO_4(s)$, plus an extra 5 mg/L SO_4^{2-} as a safety factor. What dose (mg/L) of Na_2SO_4 should be added, and what would the concentration of solids be, in ppm, if essentially all the Ba^{2+} precipitated?

3. The concentration of silver in seawater is 50 parts per trillion, and the total volume of seawater in the world's oceans is approximately $1370 \times 10^6\ \mathrm{km}^3$. The density of seawater is 1.025 kg/L.

    (a) Determine the total mass (kg) of silver in the oceans of the world.

    (b) What volume of seawater would have to be processed to recover one kilogram of silver if the extraction process were 100% efficient?

4. The partial pressure of carbon dioxide in air is approximately $10^{-3.42}$ atm. In temperate regions, P_{CO_2} in soil gas can be as high as $10^{-1.5}$ atm. For each of these two cases, calculate the mass of carbon dioxide (in grams) in 1.0 m^3 of gas at $T = 25°C$.

5. The partial pressures of nitrogen (N_2) and oxygen (O_2)in air are 0.78 atm and 0.21 atm, respectively. Calculate the number of moles and the mass (mg) of each of these components in 1 L of air at 25°C.

6. Ozone gas (O_3) is commonly injected into drinking water (also swimming pools and hot tubs) as a disinfectant. Pure ozone decays rapidly, so it cannot be stored for long periods; as a result, it is typically generated onsite by exposing dried air to an electrical discharge that causes gaseous oxygen to be converted to ozone by the reaction: $3\,O_2(g) \longrightarrow 2\,O_3(g)$. Typically, about one-seventh of the oxygen in the gas is converted to ozone in this step.

    A water treatment plant for a city with a population of 1 million people must produce on the order of 400,000 m^3 per day of clean water. If ozone is injected into the water at a dose of 1 mg/L, what volume of air (1.0 atm total pressure, 15°C, 21% O_2) must be processed per day to provide the ozone?

7. The discharge of chromate ions (CrO_4^{2-}) to sewers or natural waters is of concern because of both its ecological impacts and its effects on human health if the receiving water is later used as a drinking water source. One way in which chromate can be removed from solution is by its reaction with ferrous ions (Fe^{2+}) to form a mixture of chromic hydroxide and ferric hydroxide solids [$Cr(OH)_3(s)$ and $Fe(OH)_3(s)$, respectively], which can then be filtered out of the water. The overall reaction can be represented as

$$\mathrm{CrO_4^{2-}} + 3\,\mathrm{Fe^{2+}} + 8\,\mathrm{H_2O} \longrightarrow \mathrm{Cr(OH)_3}(s) + 3\,\mathrm{Fe(OH)_3}(s) + 4\,\mathrm{H^+}$$

   How much particulate matter would be generated daily by this process at a facility that treats 60 m^3/h of a waste stream containing 4.0 mg/L Cr, if the treatment reduces the Cr concentration enough to meet a discharge limit of 0.1 mg/L Cr?

8. A solution contains 65 mg/L Ca^{2+} *as $CaCO_3$* and 85 mg/L alkalinity *as $CaCO_3$*. What are the Ca^{2+} concentration and the alkalinity in meq/L? What is the Ca^{2+} concentration in molar units?

9. (a) Express the concentration of Ca^{2+} in the Mississippi River near Clinton, IA (composition shown in Table **??**) in mol/L Ca^{2+} and in mg/L *as $CaCO_3$*.

   (b) Compute the ionic strength of the river water. Assume that the organic molecules are 50% C by mass, have an average molecular weight of 550, and carry an average charge of −1. Also assume that the number of equiv/L of alkalinity can be treated as the number of mol/L of HCO_3^-.

10. The following analysis has been reported for a sample of contaminated groundwater obtained near an aluminum production facility:

    pH = 11.2
    Na^+ = 6,500 mg/L
    K^+ = 2,230 mg/L
    Ca^{2+} = 3,400 mg/L
    Mg^{2+} = 1,350 mg/L
    Cl^- = 1,100 mg/L
    F^- = 4,350 mg/L
    DIC = 1,740 mg/L (*as C*)
    SO_4^{2-} = 3,940 mg/L
    OH^- = $10^{-2.8}$ mol/L

    (a) Check the charge balance for this analysis. Does the total cationic charge (in equiv/L) equal the total anionic charge to within ±5% (the typical target for an acceptable charge balance)? (Note: at pH 11.2, the inorganic carbon is predominantly in the form CO_3^{2-}.)

(b) Calculate the TDS of the solution in mg/L. Because most of the DIC is present as CO_3^{2-}, a negligible portion is released as $CO_2(g)$ during the TDS analysis.

(c) Calculate the ionic strength of the solution.

(d) Calculate the hardness of the solution in mg/L *as* $CaCO_3$.

11. The West Virginia Water Research Institute reported the following water quality measurements for the Monongahela River monitoring station at Mile 89 for August 2010.

$\mathrm{pH} = 7.79$
ALK = 59.9 mg/L *as* $CaCO_3$
$Na^+ = 44.7$ mg/L
$Ca^{2+} = 39.8$ mg/L
$Mg^{2+} = 10.6$ mg/L
$Cl^- = 15.9$ mg/L
$SO_4^{2-} = 146$ mg/L

(a) Determine the concentration of dissolved inorganic carbon (DIC) in the water in mol/L and in mg/L, assuming that HCO_3^- is the only significant contributor to ALK and DIC.

(b) Check the cation–anion balance for this analysis.

(c) Calculate the ionic strength of the solution.

(d) What is the alkalinity in meq/L, if all the alkalinity is contributed by HCO_3^- ions?

12. A natural water sample has been analyzed and reported to have the following solute concentrations.

TDS = 300 mg/L
Alkalinity = 1.5×10^{-3} equiv/L
$[Na^+] = 2.5 \times 10^{-3}\,M$
$[Ca^{2+}] = 10^{-3}\,M$
$[SO_4^{2-}] = 10^{-3}\,M$
$[Cl^-] = 0.5 \times 10^{-3}\,M$
$\mathrm{pH} = 8.2$

(a) Check the charge balance, assuming that all the alkalinity is contributed by HCO_3^-. If the charge is not balanced, determine the minimum additional concentration of sodium or chloride ions (depending on the sign of the imbalance) that would have to be present to eliminate the charge imbalance.

(b) Compare the TDS contributions of solutes that were analyzed to the reported TDS concentration. Would inclusion of the Na^+ or Cl^- ion concentration determined in part (a) resolve any discrepancy between the measured TDS and the analyses for individual ions?

13. A river contains 8 mg/L DOC in molecules whose average composition is $C_{10}H_{15}O_4N$.

    (a) What is the mass fraction of C in the organic molecules?

    (b) What are the mass fraction and mole fraction of these molecules in the solution?

14. When organic matter with an average chemical formula of $C_5H_9O_3N$ is consumed by microorganisms under aerobic conditions, it undergoes the following oxidation reaction:

$$C_5H_9O_3N + 5\,O_2 + 2\,H_2O \longrightarrow 5\,HCO_3^- + 4\,H^+ + NH_4^+$$

    If 10 mg/L DOC is consumed, how much HCO_3^- is generated? Express your answer in mg/L DIC, meq/L, and mg/L *as $CaCO_3$*.

15. What is the ionic strength of a solution containing only sodium benzoate ($NaC_7H_5O_2$) and water, if the DOC concentration in the solution is 15 mg/L? Assume that, when the sodium benzoate dissolves, it dissociates completely into sodium and benzoate ions (Na^+ and $C_7H_5O_2^-$, respectively), and that neither ion undergoes significant subsequent reactions.

16. A solution contains 30 mg/L NH_4^+ and 5 mg/L NO_3^-.

    (a) Express these concentrations as mg/L $NH_4{-}N$ and $NO_3{-}N$, respectively. Which species makes a larger contribution to the total N concentration in the water?

    (b) In biological wastewater treatment processes, conditions are sometimes established that are conducive to microbial conversion of NH_4^+ to NO_3^- (nitrification) in an aerobic step, and of NO_3^- to N_2 (denitrification) in a subsequent anaerobic step. What volume of $N_2(g)$ would be generated per liter of water treated if the original solution underwent complete nitrification and denitrification? Assume that the gas phase is at 25°C and 1 atm total pressure.

17. The following data summarize the concentration changes of various dissolved nitrogen species in a biological wastewater treatment process. The species listed as "organic matter" has an average composition of $C_{30}H_{33}O_{18}N$. Determine the change in total dissolved nitrogen (TDN) concentration in the process.

Species	**Influent conc'n (mg/L)**	**Effluent conc'n (mg/L)**
NH_4^+	28	4.5
NH_3	1.8	0.4
NO_3^-	0.2	95
NO_2^-	0.1	0.0
Organic matter	265	21

18. Potassium permanganate ($KMnO_4$) is sometimes added to water as it enters a drinking water treatment plant to assist in the removal of Fe^{2+} and Mn^{2+} ions. The $KMnO_4$ oxidizes those cations by acquiring electrons according to the following reaction:

$$KMnO_4 + 4H^+ + 3e^- \longrightarrow K^+ + MnO_2(s) + 2H_2O$$

   (a) What is the (electron) equivalent weight of Mn, based on this reaction?

   (b) Calculate the mass (g) of $KMnO_4$ in 2 L of a $0.15M$ $KMnO_4$ solution.

   (c) If 1.0 mL of $0.15M$ $KMnO_4$ is added to each liter of the drinking water, and all the $KMnO_4$ undergoes the reaction shown, what concentration of $MnO_2(s)$ will be generated by the reaction, in ppm?

19. You wish to add 5 mg/L NaOCl *as Cl_2* to a solution in a disinfection test, and you have a stock solution (household bleach) that contains 5% NaOCl by weight. Assuming that the density of the stock solution is 1.0 g/mL, how many milliliters of bleach should you add to each liter of test solution? The key reaction that NaOCl undergoes is

$$NaOCl + 2H^+ + 2e^- \rightleftharpoons Na^+ + H_2O + Cl^-$$

20. Calculate the normality and equivalent weight of the following species based on the reactions shown. Assume that the species concentration is 10^{-3} mol/L and that equivalency is based on charge in part (a), acid/base behavior in part (b), and oxidation/reduction behavior in parts (c) through (e).

   (a) Na^+ in: $NaCl \rightleftharpoons Na^+ + Cl^-$

   (b) Ac^- in: $HAc \rightleftharpoons H^+ + Ac^-$

   (c) Pb^{2+} in: $Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$

   (d) NO_3^- in: $NO_3^- + 2H^+ + 2e^- \rightleftharpoons NO_2^- + H_2O$

   (e) NO_3^- in: $NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$

21. After disinfection of drinking water with chlorine, the following concentrations of halogenated disinfection byproducts were found. How much TOX (μg/L *as Cl*) and how much TOC (mg C/L) are contributed by these compounds? The chemical formula of dichloroacetonitrile is Cl_2HCCN.

Species	**Conc'n (μg/L)**	**Species**	**Conc'n (μg/L)**
Chloroform	43	Dichloroacetic acid	20
Bromodichloromethane	19	Trichloroacetic acid	20
Dibromochloromethane	10	Bromoacetic acid	8
Bromoform	5	Dibromoacetic acid	15
Chloroacetic acid	10	Dichloroacetonitrile	8

22. Estimate the specific conductance at 25°C of a solution containing 700 mg/L KCl, assuming that the KCl dissociates completely. Compare your result with the estimated specific conductance of a solution of $CaSO_4$ that has the same total concentration of cationic and anionic charge as the KCl solution.

23. Consult some books on analytical chemistry to learn about two of the following analytical methods, and prepare a half-page summary of each technique. Indicate the most common units in which results of these analyses are reported. Cite the sources of your information.

    (a) atomic absorption (AA) spectroscopy for measurement of metal concentrations in water;

    (b) inductively coupled plasma (ICP) emission spectroscopy for measurement of metal concentrations in water;

    (c) selective ion electrodes for measurement of concentrations of ions such as Cu^{2+} and Cl^-;

    (d) potentiometric analysis for H^+ (pH probe).

24. Consult the APHA/AWWA/WEF reference book *Standard Methods for the Examination of Water and Wastewater* to learn about standard methods available for analysis of chloride (Cl^-) or selenium (Se). List each method and give the Standard Methods identification number and name for the method. Prepare a brief summary ($\sim$150 words) of each method, explaining how it works.

CHAPTER 2 HOMEWORK PROBLEMS

1. Compute the activities of Ca^{2+}, SO_4^{2-}, and Cl^- in the Mississippi River near Clinton, IA, using the Davies equation to estimate activity coefficients. Make the same assumptions about the composition of the organic matter as were made in Problem 9 of Chapter 1.

2. Explain briefly why we always assume that activity coefficients are 1.0 for pure solids, regardless of the ionic strength of the solution in which they are found.

3. Water in a reservoir at 20°C has a pH of 7.7 and contains the following species.

Species	**Conc'n (mg/L)**	**Species**	**Conc'n (mg/L)**
Na^+	85	SO_4^{2-}	21
K^+	5.6	Cl^-	65
Ca^{2+}	38	NO_3^-	4.0
Mg^{2+}	24	F^-	1.6
		HCO_3^-	183

   (a) Check the charge balance for this analysis by calculating the ratio of cation to anion equivalents per liter. As noted in Chapter 1, such an analysis is typically considered acceptable if the error in the charge balance, computed with Equation (1.4), is less than 5%. Is this analysis in the acceptable range?

   (b) Estimate the activities of Na^+, Ca^{2+}, and HCO_3^-, using an appropriate equation to compute the activity coefficients.

4. An aqueous solution is prepared by dissolving 100 mg/L of $CaCl_2$ and 230 mg/L of Na_2SO_4 in water. Assuming that these salts dissociate completely, and that the dissociated ions do not undergo any additional reactions, calculate

   (a) the molar concentration of each ionic species;

   (b) the ionic strength of the solution;

   (c) the activity coefficient for each species (with the Davies equation);

   (d) the activity of each species

5. What are $p[SO_4^{2-}]$ and $p\{SO_4^{2-}\}$ in solutions of $8.5 \times 10^{-6}\,M$ and $4.5 \times 10^{-3}\,M$ Na_2SO_4, assuming that the salts dissociate completely?

6. When the activity of Na^+ in an estuary is evaluated using the conventional standard state conditions (molar concentration of 1.0, chemical environment corresponding to infinite dilution in pure water), a_{Na^+} is estimated to be 0.015.

Would this value increase, decrease, or remain the same if the reference state environment were changed to infinite dilution in major-ion seawater? Explain your reasoning.

7. A solution of $0.01\,M$ $CaCl_2$ and $10^{-5}\,M$ $CuCl_2$ is prepared. Both of these salts dissociate completely when dissolved in water. If the concentration of $CaCl_2$ is then doubled, how much will the activities of Ca^{2+}, Cl^-, and Cu^{2+} change?

8. Sodium chloride is added to pure water to increase its ionic strength from essentially zero to 0.1 mol/L. The solution remains at 25° and pH 7.0 throughout the process. How many moles of water molecules dissociate per liter of solution when the salt is added? By what fraction does the concentration of H^+ increase? By what fraction does the activity of H^+ increase?

9. One gram of solid calcium sulfate [$CaSO_4(s)$] is added to 1.0 L of pure water. Some of the solid then dissolves according to the following reaction, which has an equilibrium constant of $K = 10^{-4.85}$:

$$CaSO_4(s) \rightleftharpoons Ca^{2+} + SO_4^{2-}$$

   (a) What are the concentration (mol/L) and activity of $CaSO_4(s)$ before any dissolution occurs?
   (b) What is the activity of $CaSO_4(s)$ after enough dissolution has occurred so that the reaction reaches equilibrium, assuming that not all of the solid dissolves?
   (c) Compute the concentrations of Ca^{2+} and SO_4^{2-} in mol/L and in mg/L at equilibrium, assuming that $\gamma_{Ca^{2+}} = \gamma_{SO_4^2} = \gamma_{CaSO_4(s)} = 1.0$.
   (d) Estimate the ionic strength of the solution based on the result of part (c). Then compute $\gamma_{Ca^{2+}}$ and $\gamma_{SO_4^2}$ with the Extended Debye-Hückel equation, and make a new estimate of the concentration of each ion in the equilibrated solution. Iterate between calculating the concentrations of Ca^{2+} and SO_4^{2-} and the corresponding ionic strength and activity coefficients until each calculation converges. What fraction of the original solid is dissolved at equilibrium?

10. The reactions for the dissolution of limestone ($CaCO_3(s)$) and for the dissociation of bicarbonate ion (HCO_3^-) to carbonate ion (CO_3^{2-}) are as follows:

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K = 10^{-8.3}$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K = 10^{-10.33}$$

These reactions have reached equilibrium in a solution at pH 9.33 that contains 10^{-2} mol/L $CaCO_3(s)$ and $10^{-3.3}$ mol/L Ca^{2+}.

(a) What is the HCO_3^- concentration in the solution, assuming that activity coefficients for all species are 1.0?

(b) Would you expect the Ca^{2+} concentration to increase, decrease, or not change if the system changed in the following ways? For this part of the problem, do not assume that activity coefficients are 1.0. In each case, explain your reasoning briefly (1-2 sentences). For this part of the question, consider only the effect on the first reaction shown above.

  (i) The concentration of $CaCO_3(s)$ is doubled.

  (ii) The ionic strength of the solution increases, e.g., by addition of NaCl.

  (iii) The pH is lowered slightly, without significantly altering the ionic strength.

11. Having become thoroughly frustrated with the concept of moles, a group of reformers decides to defy convention and carry out all calculations using a new set of definitions for the standard state. They choose the standard state concentration to be 1 mg/L for all solutes and 1000 g/L for water, but they retain the conventional reference state conditions of infinite dilution for solutes and pure liquid water for H_2O. The equilibrium constant for the following reaction using the conventional standard state definitions is $10^{11.32}$. Compute the equilibrium constant using the revised conventions. Include dimensions, if appropriate.

$$H_2CO_3 + 2\,OH^- \rightleftharpoons CO_3^{2-} + 2\,H_2O$$

CHAPTER 3 HOMEWORK PROBLEMS

1. An elementary reaction $A \rightleftharpoons B$ has an equilibrium constant of 10, and a forward rate constant of 1.0 d^{-1}.

    (a) Plot the concentrations of A and B as a function of time in a batch reactor that initially contains $10^{-3}\,M$ each of A and B. Show the data from the initial condition until the concentrations are changing at an instantaneous rate of less than $10^{-5}\,M$ per day.

    (b) Repeat part (a) if the initial concentrations are $2 \times 10^{-3}\,M$ A and no B.

    (c) What are the molar concentrations of A and B at equilibrium in part (b)?

2. The reaction $2\,A \rightleftharpoons B + C$ is elementary in both directions and has an equilibrium constant of 75. In a batch solution that contains 10 mmol/L A and no B or C, the initial rate of reaction generates 0.3 mmol B per liter per minute. What is the net rate of formation of B under conditions where the concentrations of A, B, and C are 2, 10, and 10 mmol/L, respectively?

3. A reversible reaction that is elementary in both directions has the following stoichiometry:

    $$A + B \rightleftharpoons 2P$$

    Hydroxide ion has been found to catalyze (i.e., to increase the rate of) the forward reaction. How would the following parameters change when the pH is increased? Briefly explain your reasoning.

    (a) The activation energy for the forward reaction.

    (b) The rate constant for the reverse reaction.

4. Two reversible, elementary reactions proceed in the following sequence:

    $$A + B \rightleftharpoons 2C \rightleftharpoons D + E$$

    The rate constants for the reactions are as follows, where '1' and '2' refer to the first and second reaction, respectively:

    $$k_{1,\mathrm{f}} = 0.04\,M^{-1} \cdot \mathrm{s}^{-1} \qquad k_{1,\mathrm{r}} = 0.01\,M^{-1} \cdot \mathrm{s}^{-1}$$

    $$k_{2,\mathrm{f}} = 0.10\,M^{-1} \cdot \mathrm{s}^{-1} \qquad k_{2,\mathrm{r}} = 0.10\,M^{-1} \cdot \mathrm{s}^{-1}$$

    (a) If a solution initially contains 60 mmol/L of A, 40 mmol/L of B, and no C, D, or E, what will the distribution of species be at equilibrium? (Hint: the equilibrium solution composition comprises five unknowns [the concentrations of the five species], which can be determined by writing and solving five independent equations involving those unknowns. The available equations include mass balances that characterize the stoichiometry of the reactions, and equilibrium constant expressions. Try to write and solve five independent equations that characterize the system.)

(b) What is the equilibrium constant for the reaction $0.5\text{A} + 0.5\text{B} \rightleftharpoons \text{C}$?

5. A network of elementary reactions is shown below, along with rate constants for the forward (f) and reverse (r) of each reaction. Note that species A is consumed in reactions 1 and 2 and is then generated in reaction 3. Similarly, species D is generated in reaction 2 and then consumed in reaction 3. The rate constants apply when the species' activities (not their concentrations) are used in the reaction rate expressions. The units of 'mol' refer to moles of stoichiometric reaction.

$$\begin{array}{rll}
\text{A}+\text{B} \rightleftharpoons \text{C}+\text{H}_2\text{O} & k_{\text{f},1} = 6.6\times10^{-3}\ \text{mol/L·s}, & k_{\text{r},1} = 3\times10^{-11}\ \text{mol/L·s} \\
2\,\text{A}+\text{C} \rightleftharpoons \text{D} & k_{\text{f},2} = 4.0\times10^{-5}\ \text{mol/L·s}, & k_{\text{r},2} = 1\times10^{-9}\ \text{mol/L·s} \\
\text{D}+\text{H}_2\text{O} \rightleftharpoons \text{E}+\text{A} & k_{\text{f},3} = 2\times10^{-7}\ \text{mol/L·s}, & k_{\text{r},3} = 0.10\ \text{mol/L·s}
\end{array}$$

(a) Write the overall reaction corresponding to the sum of these elementary reactions and determine the equilibrium constant that applies to that reaction.

(b) A system that contains all the species that participate in these reactions has reached equilibrium. Do you think any of the elementary reactions can be treated as irreversible under these conditions? Why or why not?

6. The data below summarize the loss of a solute from water due to a chemical reaction in a batch reactor. Determine whether the data are best fit by a zero-order, first-order, or second-order rate expression, and report the rate constant with proper units.

Time (h)	Conc'n (mg/L)
0	100
0.5	27.0
1.0	11.1
2.0	6.5
3.0	3.7
5.0	2.3

7. The following data were collected in a laboratory batch experiment investigating the degradation of a contaminant in a water treatment process. Are the data consistent with an n^{th}-order reaction rate? If so, what are the values of n and the rate constant? [Hint: Derive an equation that approximates the given c vs. t data, and then use that equation to estimate the half-time for several different initial concentrations. Then, apply Equation (3.35) to see if the data fit an n^{th}-order rate expression.]

Time (min)	Conc'n (μM)	Time (min)	Conc'n (μM)
0	250	35	105
5	220	40	100
10	200	45	90
15	170	50	75
20	155	55	70
25	145	60	60
30	130		

8. The radionuclide ^{32}P has a half-life of 14.3 days. How long would an aqueous waste containing 1.0 mg/L of this nuclide have to be stored to reduce the concentration to 0.03 mg/L through radioactive decay?

9. The following reaction is elementary but is reported to be "pseudo-first-order" with a rate constant of $10^{-1}\,\mathrm{s}^{-1}$.

$$\mathrm{CO_2}(aq) + \mathrm{H_2O} \longrightarrow \mathrm{H_2CO_3}$$

   Explain why the reaction is pseudo-first-order, even though it requires a collision between two molecules. Present an appropriate equation to support your explanation.

10. The decomposition of ozone in water fits the general rate equation

$$r_{\mathrm{O_3}(aq)} = -k_{\mathrm{d}}\left[\mathrm{O_3}\,(aq)\right]^a \left[\mathrm{OH^-}\right]^b$$

   Staehelin and Hoigne (1982)[1] reported the data in the following table for the decrease in the $\mathrm{O_3}(aq)$ concentration over time at pH=10 in batch reactors.

Expt 1*		Expt 2		Expt 3	
$[\mathrm{O_3}]$	Time	$[\mathrm{O_3}]$	Time	$[\mathrm{O_3}]$	Time
0	12.00	0	3.00	0	0.330
15	8.76	10	2.49	10	0.261
30	6.36	30	1.77	20	0.225
45	5.04	40	1.50	30	0.180
60	4.08	50	1.23	40	0.159
75	3.24	60	1.02	50	0.123
90	2.16	70	0.90	60	0.114
		80	0.75	80	0.075
		90	0.63		

* In all experiments, the units for $[\mathrm{O_3}]$ and time are μM and s, respectively.

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[1] Staehelin, J., and Hoigne, J. (1982) "Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide." *Environ. Sci. Technol. 16*, 676-681.

(a) Determine the order of the reaction with respect to $O_3(aq)$.

(b) Write the rate equation and evaluate k_d, assuming $b = -1$.

(c) Still assuming that $b = -1$, estimate the pseudo-first-order rate constant for ozone decay at fixed pH values of 8.0, 9.0, and 10.0. What is the half-life of ozone in water at each of these pH's?

11. Consider the following irreversible reaction for conversion of chlorophenol (C_6H_4OHCl, or 'CP') to dioxin [$(C_6H_3ClO)_2$].

$$2\,C_6H_4OHCl + 0.5\,O_2(aq) \longrightarrow (C_6H_3ClO)_2 + H_2O$$

$$r_\text{CP} = -k[\text{CP}]^2[O_2\,(aq)]^{0.5}$$

If $k = 10\ \text{L}^{1.5}/(\text{mol}^{1.5}\cdot\text{s})$, how long would be required to form $10^{-9}\,M$ dioxin in a batch reactor if the initial solution contained $10^{-7}\,M$ chlorophenol and $[O_2(aq)]$ was maintained at $2.5\times10^{-4}\,M$?

12. At pH below about 3.5, ferrous iron (Fe^{2+}) oxidizes in streams according to the following overall reaction:

$$Fe^{2+} + 0.25\,O_2(aq) + H^+ \rightleftharpoons Fe^{3+} + 0.5\,H_2O$$

The rate law for the abiotic oxidation of ferrous iron under these conditions and at 20°C is

$$r_{Fe^{2+}} = -k\left[Fe^{2+}\right]P_{O_2}$$

where P_{O_2} is the partial pressure of gas-phase oxygen that is in equilibrium with the solution, and $k = 10^{-3.2}\ \text{atm}^{-1}\cdot\text{s}^{-1}$.

Calculate the time required for the concentration of Fe^{2+} to be reduced to 1% of its initial concentration in a batch reactor where the solution is in continuous equilibrium with the atmosphere.

13. When chlorine is added to water containing ammonia, chloramine compounds (NH_xCl_{3-x}, with x=0, 1, or 2) form. Monochloramine (NH_2Cl) can split ('disproportionate') into dichloramine and ammonia according to the following reaction and rate expression:

$$2\,NH_2Cl \longrightarrow NHCl_2 + NH_3 \qquad\qquad r_{NH_2Cl} = -k(NH_2Cl)^2$$

If $k = 20\,M^{-1}\cdot\text{s}^{-1}$, what will the monochloramine concentration be 10 min after chlorine is added, if the concentration immediately after dosing is 0.1 mM and no more NH_2Cl forms thereafter?

14. Hypochlorous acid (HOCl) can react with ferrous iron (Fe^{2+}) to produce ferric iron (Fe^{3+}) via the following reaction:

$$2\,\mathrm{Fe}^{2+} + \mathrm{HOCl} \longrightarrow 2\,\mathrm{Fe}^{3+} + \mathrm{Cl}^- + \mathrm{OH}^-$$

Two experiments are carried out with solutions that initially contain $0.01\,M$ Fe^{2+}, no Fe^{3+}, and $10^{-3}\,M$ HOCl. In one, conducted at 10°C, the concentration of Fe^{3+} generated in 1 minute is $1.0 \times 10^{-5}\,M$. When the temperature is increased to 20°C, $2.4 \times 10^{-5}\,M$ Fe^{3+} is generated in one minute. Assuming the rate expression has the following form, calculate the rate constant at each temperature and estimate the activation energy for the reaction.

$$r_{\mathrm{Fe}^{3+}} = k\left[\mathrm{Fe}^{2+}\right]^2[\mathrm{HOCl}]$$

15. The hydrolysis of pyrophosphate can be described by the reaction

$$\mathrm{H_2PO_7^{2-}} + \mathrm{H_2O} \longrightarrow 2\,\mathrm{H_2PO_4^-}$$

If the pH is held constant, the reaction is pseudo-first order with respect to $\mathrm{H_2PO_7^{2-}}$.

(a) If, at a given pH, the half-life of pyrophosphate is 140 h at 75°C and 13 h at 100°C, what is E_{Ar} for the reaction?

(b) Estimate the time required for 50% hydrolysis of pyrophosphate in a solution at the same pH as in part (a), but at 20°C.

16. In the presence of dissolved oxygen, microorganisms can oxidize nitrite ions ($\mathrm{NO_2^-}$) to nitrate ions ($\mathrm{NO_3^-}$) via the following reaction:

$$\mathrm{NO_2^-} + 0.5\,\mathrm{O_2}(aq) \longrightarrow \mathrm{NO_3^-}$$

(a) This reaction is occurring in a batch bioreactor at a rate that is first order with respect to both $\mathrm{NO_2^-}$ and $\mathrm{O_2}(aq)$, with $k_2 = 3 \times 10^4$ L/mol·d. How much time is required for the nitrite concentration to be reduced from 0.3 mM to 0.1mM if $\mathrm{O_2}$ is resupplied continuously to maintain the $\mathrm{O_2}(aq)$ concentration at 4 mg/L?

(b) Repeat part (a), but assume that $\mathrm{O_2}$ is not resupplied, so that the $\mathrm{O_2}(aq)$ concentration is initially 4 mg/L but declines as the reaction proceeds.

17. The stoichiometry of the reaction of hydrogen sulfide with dissolved oxygen is given by

$$\mathrm{H_2S}(aq) + 2\,\mathrm{O_2}(aq) \longrightarrow \mathrm{SO_4^{2-}} + 2\,\mathrm{H}^+$$

Millero et al. (1987)[2] reported that, at pH < 7 and 25°C, this reaction is first order with respect to both $\mathrm{H_2S}$ and $\mathrm{O_2}$, with a rate constant of $k = 11$ L/mol·h.

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[2] Millero, F.J., Hubinger, S., Fernandez, M., and Garnett, S. (1987) "Oxidation of $\mathrm{H_2S}$ in seawater as a function of temperature, pH, and ionic strength." *Environ. Sci. Technol. 21*, 439-443.

Consider a solution containing $10^{-5}\,M$ $H_2S(aq)$ and a constant dissolved oxygen concentration of 0.25 mM (8.0 mg/L). If the given reaction is the only way that sulfide is lost from the system, how much dissolved sulfide will remain after one day at pH 5? (As is explained in Chapter 5, at pH 5.0, $H_2S(aq)$ accounts for virtually all the dissolved sulfide in the system.)

18. In the biochemical oxygen demand (BOD) test, a sample of water is inoculated with microorganisms and then incubated with essential nutrients to determine how much dissolved oxygen is consumed by the constituents in the sample under conditions favorable for microbial growth. The rate of oxygen consumption is typically modeled as first-order with respect to the concentration of dissolved oxygen that *could be consumed* by reaction with other constituents present in the solution; this parameter is conventionally represented as L. Thus:

$$r_{O_2} = -k_1 L$$

A BOD bottle is filled with 270 mL of treated wastewater plus 30 mL of 'dilution water' containing the bacterial seed and nutrients. The constituents in the treated wastewater have the potential to consume a maximum of 15 mg/L of oxygen. (This value is known as the *ultimate BOD* of the sample, L_0.) How long can the solution be incubated before the dissolved oxygen concentration decreases to 1.0 mg/L if the constituents in the dilution water consume almost no oxygen, the mixture of sample and dilution water initially contains 10.5 mg/L dissolved oxygen, and the rate constant for oxygen consumption is 0.45 d^{-1}?

19. N-nitrosodimethylamine (NDMA) is a suspected carcinogen that can form via reactions between dimethylamine (DMA) and monochloramine (NH_2Cl). DMA is a precursor for the formation of many industrial chemicals and can enter water supplies as a contaminant in polymers that are used in water treatment. NH_2Cl is frequently generated intentionally in water supplies during water treatment operations, because it can disinfect water without forming chlorinated disinfection byproducts (DBPs). Choi and Valentine (2002)[3] suggested that the relevant elementary reactions and the corresponding rate constants are as shown below.

Reaction	Rate Constant ($M^{-1}\cdot s^{-1}$)
$DMA + NH_2Cl \rightleftharpoons DMCA + NH_3$	$k_f = 1.4\times10^{-1}$, $k_r = 5.83\times10^{-3}$
$DMA + NH_2Cl \longrightarrow UDMH$	1.28×10^{-3}
$UDMH + NH_2Cl \longrightarrow NDMA$	1.11×10^{-1}

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[3] Choi,J., and Valentine, R.L. (2002) "Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product." *Water Research 36*, 817-824.

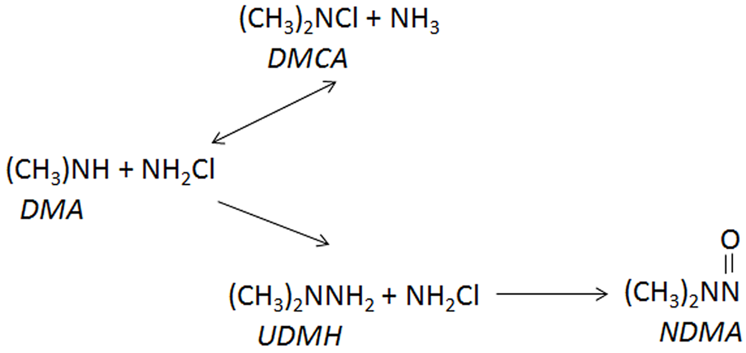

Figure 3.13. Reaction pathway for formation of NDMA from DMA and monochloramine.

Predict the concentrations of all species that participate in these reactions as a function of time for 500 hours in a batch experiment with initial concentrations of 10^{-5} *M* DMA, 10^{-4} *M* NH_2Cl, 2×10^{-5} *M* NH_3, and zero for the other species shown. Explain the concentration trends qualitatively.

20. The Chick-Watson model characterizes the rate of inactivation of microorganisms by disinfectants. The model indicates that, for a given type of organism, disinfectant, pH, and temperature,

$$\ln(N_t/N_0) = -\Lambda c^n t$$

where N_t is the concentration of living organisms at time t, c is the concentration of disinfectant, and Λ and n are constants. (These constants are sometimes referred to, respectively, as the coefficient of specific lethality and the coefficient of dilution.) The value of n is often approximately 1.0. The following values of Λ were reported by Scarpino et al. (1974)[4] for inactivation of *E. coli* and poliovirus by HOCl and OCl^- (the active ingredients in bleach) when c is in mg/L *as* Cl_2 and t is in seconds.

Disinfectant	*E. coli* bacteria	Poliovirus 1
HOCl	1.64	0.042
OCl^-	0.088	0.20

(a) For a water at pH 7.5 that contains $10^{-4.5}$ $M\ TOT$OCl, calculate the concentrations of HOCl and OCl^- in mol/L and in mg/L *as* Cl_2. (Hint: use the approach shown in Example 2.6 to determine the relative concentrations of HOCl and OCl^-.)

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[4] Scarpino, P.V., Lucas, M., Dahling, D.R., Berg, G., and Chang, S.L. "Effectiveness of hypochlorous acid and hypochlorite ion in destruction of viruses and bacteria." Chapter 15 *in* Chemistry of Water Supply, Treatment, and Distribution. A.J. Rubin, ed. Ann Arbor Science (Ann Arbor, MI) (1974).

(b) Plot $\log(N/N_0)$ vs. time (in seconds) for *E.coli* and for Poliovirus 1, for the solution described in part (a). Assume that $n = 1$, the disinfectant concentrations are approximately constant and that the effects of HOCl and OCl^- are additive. How long is required to reduce the population of each organism by a factor of one million?

21. Fine particles suspended in water can collide as a result of differential settling rates, fluid mixing, and/or Brownian motion. Under certain conditions, these collisions cause the particles to aggregate into larger particles which are more likely than the original particles to settle out of the water column. By itself, the aggregation process reduces the number concentration of suspended particles (i.e., number of particles per unit volume of solution), but not the mass concentration.

    Aggregation is sometimes modeled as an irreversible rate process with second order dependence on the number concentration of suspended particles. Consider a suspension that initially contains 10^8 particles per liter and in which the rate constant for aggregation is 5×10^{-10} L/particle·s.

    (a) Determine the number concentration of particles remaining in suspension after 30 min.

    (b) How long would be required for the particle concentration to decline to 10^5 /L?

22. In the early sanitary engineering literature, there was a great deal of interest in the effect of temperature on the rates of biodegradation and oxygen transfer in aquatic systems, where the range of temperatures is limited to around $20 \pm 20°\text{C}$ (293 ± 20 K). Based on that work, an empirical model was developed suggesting that

$$\frac{k_{T_2}}{k_{T_1}} = \theta^{T_2 - T_1}$$

    where θ is an empirical constant. Typically, the value of k at $T_1 = 20°\text{C}$ was determined in the laboratory, and its value at other temperatures was estimated from the preceding equation. For T in °C or Kelvins, commonly cited values of θ were 1.047 for utilization of oxygen by microorganisms (BOD consumption) and 1.016 for oxygen transfer from the atmosphere to water. Compare the expressions for the temperature dependence of these two reactions to the Arrhenius equation and estimate E_{Ar} for each reaction.

CHAPTER 4 HOMEWORK PROBLEMS

1. Calculate the standard Gibbs energy of reaction and the equilibrium constant at 25°C for the following reactions:

   (a) $Fe^{3+} + 3\,OH^- \rightleftharpoons Fe(OH)_3(s)$

   (b) $Mg^{2+} + OH^- \rightleftharpoons MgOH^+$

   (c) $Ca^{2+} + SO_4^{2-} + 2\,H_2O \rightleftharpoons CaSO_4{\cdot}2\,H_2O(s)$

   (d) $HAsO_4^{2-} + H^+ \rightleftharpoons H_2AsO_4^-$

2. Calculate $\Delta\overline{G}_r^\circ$ for the dissolution of ferrous hydroxide [$Fe(OH)_2(s)$] into Fe^{2+} and OH^- ions. If an ideal solution containing 2 mg/L Fe^{2+} and 10 mg/L of the solid is at pH 7.0, in which direction will the reaction proceed?

3. When a piece of metal is exposed to a strong acid, the metal corrodes and gas bubbles are sometimes formed. These gas bubbles are pure hydrogen (H_2), and indicate that the partial pressure for $H_2(g)$ in the system is 1.0 atm. For example, if the metal is lead, the reaction would be

   $$Pb(s) + 2H^+ \rightleftharpoons Pb^{2+} + H_2(g)$$

   The Gibbs energy of this reaction is −9.06 kJ/mol when the pH is 4.0, the Pb^{2+} concentration is 1 mg/L, and hydrogen bubbles are forming on the surface of the $Pb(s)$. Use this information to find the equilibrium constant for the reaction.

4. Consider systems where the following reactions are occurring under the conditions indicated:

   (i) $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$;

   $$[H_2PO_4^-] = 10^{-3}M,\ [HPO_4^{2-}] = 5\times10^{-3}M,\ \text{pH} = 7.0,\ I = 0M$$

   (ii) $Hg^{2+} + 2\,Cl^- \rightleftharpoons HgCl_2(aq)$;

   $$[Hg^{2+}] = 10^{-7}M,\ [HgCl_2(aq)] = 10^{-6}M,\ [Cl^-] = 0.5M,\ I = 0.5M$$

   (iii) $NH_3(g) + H^+ \rightleftharpoons NH_4^+$;

   $$P_{NH_3(g)} = 10^{-6}\,\text{atm},\ [NH_4^+] = 10^{-6}M,\ \text{pH} = 9.0,\ I = 0.008M$$

   (iv) $Cd(OH)_2(s) \rightleftharpoons Cd^{2+} + 2\,OH^-$;

   $$[Cd(OH)_2(s)] = [Cd^{2+}] = 10^{-4}M,\ \text{pH} = 6.5,\ I = 0.05M$$

For each reaction:

(a) Use thermodynamic data to determine the equilibrium constant, K, at $T = 25°\text{C}$.

(b) Would the reaction be more likely to proceed to the right, to the left, or neither, with increasing ionic strength?

(c) Calculate the Gibbs energy of reaction in kJ/mol for the conditions specified. Use the Davies equation to calculate activity coefficients.

5. (a) Determine the standard Gibbs energy of reaction and the equilibrium constant for the following reactions:

   (i) $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+ + \text{Br}^-$
   (ii) $\text{PO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{HPO}_4^{2-}$
   (iii) $\text{HPO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{PO}_4^-$
   (iv) $\text{PO}_4^{3-} + 2\,\text{H}^+ \rightleftharpoons \text{H}_2\text{PO}_4^-$
   (v) $\text{AgBr}(s) + \text{Cl}^- \rightleftharpoons \text{AgCl}(s) + \text{Br}^-$
   (vi) $\text{AgCl}(s) + \text{Br}^- \rightleftharpoons \text{AgBr}(s) + \text{Cl}^-$

   (b) A solution contains $10^{-2}M$ Cl^-, $10^{-5}M$ Ag^+, and $10^{-6}M$ $\text{AgCl}(s)$ initially. Is the reaction for precipitation of $\text{AgCl}(s)$ from Ag^+ and Cl^- at equilibrium? If not, what is the Gibbs energy of reaction for formation of more $\text{AgCl}(s)$ under these conditions? What reaction will occur spontaneously? Find the concentrations of all the species, including the solid, when equilibrium is attained. Assume all activity coefficients are unity.

6. Find $\Delta\overline{G}_r^\circ$ and K for the following reaction for conversion of solid calcite to lime and carbon dioxide. $\overline{G}^\circ_{\text{CaO}(s)} = -604.0\,\text{kJ/mol}$.

$$\text{CaCO}_3(\text{calcite}) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

A dry mixture containing 1 g of each calcite and $\text{CaO}(s)$ is in contact with the atmosphere. Does the thermodynamic driving force favor conversion of one of the solids into the other, or are the solids equilibrated with one another?

7. (a) Use thermodynamic data to determine the equilibrium constants at 25°C for the following reactions. $\overline{G}^\circ_{\text{H}_3\text{SiO}_3^-} = -1260.5\,\text{kJ/mol}$.

$$\text{am-SiO}_2(s) + 2\,\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$$
$$\text{am-SiO}_2(s) + 2\,\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+$$

   (b) Both of the above reactions are at equilibrium in an aqueous system at pH= 8.0 and 25°C. What are the concentrations of H_4SiO_4 and H_3SiO_4^- in the solution, if the solutes behave ideally?

   (c) Repeat part (b) for pH= 10.0.

   (d) Considering possible nonideal solute behavior, if the ionic strength of the solution in part (c) were increased at constant pH, would some am-$SiO_2(s)$ dissolve, would more am-$SiO_2(s)$ form, or would the amount of am-$SiO_2(s)$ in the system remain steady?

8. The oxidation of Mn^{2+} by dissolved oxygen can yield the manganese dioxide [$MnO_2(s)$] mineral pyrolusite, as indicated below:

$$\mathrm{Mn^{2+}} + 0.5\,\mathrm{O_2}(aq) + \mathrm{H_2O} \rightleftharpoons \mathrm{MnO_2}(s) + 2\mathrm{H^+}$$

   Calculate the maximum 'useful' energy theoretically available per mole of stoichiometric reaction under the following conditions: $[\mathrm{Mn^{2+}}] = 1.0 \times 10^{-5}\,M$; 8.0 mg/L dissolved oxygen; pH $= 7$. Assume that the ionic strength of the water is low.

9. Why is it typically more convenient to predict the direction of a reaction in terms of Gibbs energies of the constituents rather than entropies, even though the most universal statement of the second law of thermodynamics is expressed in terms of entropy?

10. When a gas phase containing ammonia [$NH_3(g)$] comes in contact with water, some ammonia can dissolve, forming $NH_3(aq)$. The equilibrium constant for the reverse of this reaction (i.e., transfer of dissolved ammonia to the gas phase) is referred to as Henry's constant for ammonia ($H_{\mathrm{NH_3}}$, not to be confused with the molar enthalpy of ammonia, $\overline{H}_{\mathrm{NH_3}}$) and is discussed extensively in Chapter 9. Once in solution, $NH_3(aq)$ can combine with an H^+ ion to form ammonium ions (NH_4^+). These reactions can be represented as follows:

$$\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{NH_3}(g) \qquad K = H_{\mathrm{NH_3}}$$

$$\mathrm{NH_3}(aq) + \mathrm{H^+} \rightleftharpoons \mathrm{NH_4^+} \qquad K = 10^{9.24}$$

   A solution at pH 7.0 is in equilibrium with $NH_3(g)$ at a partial pressure of $10^{-6.0}$ atm. The pH is then rapidly lowered to 6.0. Assuming that the NH_3/NH_4^+ reaction equilibrates instantaneously, but that the exchange of NH_3 between the gas and solution does not, compute the following values.

   (a) $H_{\mathrm{NH_3}}$.

   (b) $\Delta\overline{G}_r$ for the dissolution of $NH_3(g)$ prior to the change in pH.

   (c) The concentrations of $NH_3(aq)$ and NH_4^+ in the original solution.

   (d) The concentrations of $NH_3(aq)$ and NH_4^+ after the pH has been lowered, but before any NH_3 has been transferred between the gas and solution. (Hint: Follow the approach used in Example 2.6, where the concentrations of HOCl and OCl^- were determined as a function of pH for a solution with known TOTOCl.)

(e) $\Delta\overline{G}_r$ for the dissolution of $NH_3(g)$ for the same conditions as in part (d). Will $NH_3(g)$ transfer into or out of the water after the pH change?

11. A resort has a swimming pool that is kept at 25°C and a hot tub that is kept at 40°C. The water in both facilities contains $2 \times 10^{-4}\,M$ total hypochlorite (TOTOCl, the sum of the HOCl and OCl^- concentrations) and is adjusted to pH 7.2 $\left(a_{H^+} = 10^{-7.2}\right)$.

    (a) The equilibrium constant for the dissociation of HOCl into H^+ and OCl^- in the swimming pool is $10^{-7.53}$. What is its value in the hot tub?

    (b) What is the concentration of HOCl (the more powerful of the two disinfectant species) in each solution, if the solutes behave ideally?

12. Compute K for the dissolution of oxygen from the atmosphere ($P_{O_2} = 0.21$ atm) into a lake under winter (3°C) and summer (28°C) conditions. The reaction can be represented as: $O_2(g) \rightleftharpoons O_2(aq)$. What is the equilibrium concentration of dissolved O_2 in mg/L under each condition?

13. Under a given set of conditions, $\Delta\overline{G}_r$, $\Delta\overline{G}_r^\circ$ and K_{eq} for the following reaction are determined to be -21.0 kJ/mol, 19.41 kJ/mol, and $10^{-3.40}$, respectively.

$$2\,Cr^{3+} + 3\,HOCl + 5\,H_2O \rightleftharpoons 2\,CrO_4^{2-} + 13\,H^+ + 3\,Cl^-$$

What are the values of those three parameters for the same conditions if the reaction is written such that it involves only one Cr^{3+} ion (i.e., with all the stoichiometric coefficients divided by 2)? Will the reaction proceed from left to right, from right to left, or will it not proceed in either direction? Explain briefly.

14. The equilibrium constant for the dissociation of hydrogen sulfide (H_2S) to bisulfide ion (HS^-) at 25°C is $10^{-7.02}$. Calculate the equilibrium constant for this reaction from 0°C to 30°C in 5°C increments and plot $\log K$ vs. T. Does dissociation of H_2S become more or less favorable as temperature increases?

15. When a solid PQ(s) is added to distilled water at 25°C, $10^{-5.0}$ mol/L of the solid dissolves, releasing P^+ and Q^- ions. When the same experiment is carried out at 15°C, only one-half as much dissolves. How much solid will dissolve if it is added to a solution at 30°C that already contains $10^{-5}\,M$ P^+ and no Q^-?

16. Determine the equilibrium constant for dissolution of covellite [CuS(s)] by the following reaction at 5, 25, and 35°C.

$$CuS(s) + H^+ \rightleftharpoons Cu^{2+} + HS^-$$

17. In the 1990's, the Boeing Co. developed a process for treating wastewater from electroplating and printed circuit board manufacturing. The central feature of the process was addition of scrap aluminum metal to an acidic solution containing dissolved copper ions. If the solution contained enough fluoride or chloride ions, a reaction proceeded in which the aluminum dissolved and the copper precipitated as metallic Cu(s), which could then be removed from the suspension by settling and/or filtration. The relevant reaction can be written as follows:

$$3\,\mathrm{Cu}^{2+} + 2\,\mathrm{Al}(s) \rightleftharpoons 3\,\mathrm{Cu}(s) + 2\,\mathrm{Al}^{3+}$$

If a wastewater initially containing 300 mg/L Cu^{2+} and no dissolved aluminum is dosed with 100 mg/L of Al scraps and the above reaction proceeds until equilibrium is reached, what will the final concentrations of Cu^{2+}, Al^{3+}, Cu(s), and Al(s) be?

18. The following three reactions all describe the conversion of gas-phase hydrogen and oxygen into H_2O, with the water being liquid in two cases and a gas in the third. The equilibrium constant for Reaction 1 at 25°C is $K = 10^{41.56}$. The partial pressures of $H_2(g)$ and $O_2(g)$ in the earth's atmosphere are 5×10^{-7} atm and 0.21 atm, respectively.

$$\begin{aligned}
&\text{Reaction 1:} \quad \mathrm{H_2}(g) + 0.5\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{H_2O}(l)\\
&\text{Reaction 2:} \quad 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{H_2O}(l)\\
&\text{Reaction 3:} \quad \mathrm{H_2}(g) + 0.5\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{H_2O}(g)
\end{aligned}$$

   (a) Is Reaction 1 thermodynamically favorable under normal atmospheric conditions?

   (b) Under a given set of conditions, is the magnitude of $\Delta\overline{G}_r$ for Reaction 2 larger, smaller, or the same as $\Delta\overline{G}_r$ for Reaction 1? Explain your reasoning.

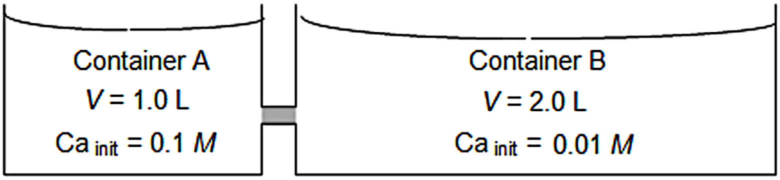
19. The following reaction for conversion of butyrate ions to acetate ions plays a central role in the anaerobic degradation of organic wastes. The standard Gibbs energy of formation of butyrate is −352.6 kJ/mol.

$$\mathrm{C_4H_7O_2^-} + 2\,\mathrm{H_2O} \longrightarrow 2\,\mathrm{C_2H_3O_2^-} + 2\,\mathrm{H_2}(g) + \mathrm{H}^+$$

   (a) Determine the molar Gibbs energy of the reaction in a solution at pH 7 in which the acetate and butyrate concentrations are both 0.01 M, if $P_{\mathrm{H_2}(g)}$ is 5×10^{-6} atm. Assume that the solutes behave ideally.

   (b) Calculate the partial pressure of $H_2(g)$, in atm, that would be required for the reaction to be in equilibrium for the solution conditions described in part (a).

20. Consider two containers (A and B) containing Ca^{2+} ions dissolved in 1.0 L and 2.0 L of water, respectively. The initial Ca^{2+} concentrations are $0.1\,M$ in container A and $0.01\,M$ in container B. The system is shown schematically in the figure below. Assuming that both solutions behave ideally, compute $\overline{G}_{\mathrm{Ca}^{2+}}$ in each container as a function of the mass of Ca^{2+} that diffuses from A to B, and use the results to determine the distribution of the Ca^{2+} at equilibrium. (Note: in theory, water would also diffuse from one side of the system to the other, since its chemical potential is slightly different on the two sides of the system. However, we can ignore this small transfer and assume that the volumes of water in the two containers are constant.)



21. Most bacteria are able to oxidize simple organic compounds, converting the carbon in the compounds to carbonic acid (H_2CO_3) or bicarbonate ions (HCO_3^-) and capturing the energy released by the reactions to carry out metabolic functions like food capture, waste elimination, and synthesis of new biomass. The chemical transformation of the carbon from its original form to species of the carbonate group is typically the same regardless of the other reactants that participate in the reaction or the overall solution composition. However, these latter factors place major constraints on the types of bacteria that can mediate the reaction and the amount of energy that can be acquired from the reaction. For example, most bacteria that can eat the organic matter by mediating a reaction between the organics and sulfate cannot survive if even a small amount of dissolved oxygen is present. Also, although some bacteria can mediate reactions of organic matter with either oxygen or nitrate, the amount of energy that they can obtain differs depending on which reactant is used.

    Consider three solutions containing methanol (CH_3OH) as the major organic constituent, along with the inorganic constituents listed below. Determine the maximum amount of energy that bacteria could acquire by oxidizing the methanol based on each of the reactions shown. (Keep in mind that different bacteria would proliferate depending on the solution composition; no single bacterial species could mediate all three reactions. In fact, as noted above, bacteria that mediate the reaction with sulfate could not even survive in Solution 1.) $\overline{G}^{\circ}_{\mathrm{N}_2(aq)} = -18.23$ kJ/mol.

	Solution 1	**Solution 2**	**Solution 3**
pH	7.3	7.3	7.3
HCO_3^- (equiv/L)	0.004	0.004	0.004
O_2 (mg/L)	3.0	0	0
NO_3^-–N (mg/L)	15	15	0
N_2 (mg/L)	8	8	8
SO_4^{2-} (mg/L)	85	85	85
HS^- (mg/L *as S*)	0	0	1
TOC (mg/L, assumed to be CH_3OH)	350	350	350

$$\begin{aligned}
&\text{Reaction 1:}\quad CH_3OH + 1.5\,O_2(aq) \longrightarrow HCO_3^- + H_2O + H^+ \\
&\text{Reaction 2:}\quad CH_3OH + 1.2\,NO_3^- + 0.2\,H^+ \longrightarrow HCO_3^- + 0.6\,N_2(aq) + 1.6\,H_2O \\
&\text{Reaction 3:}\quad CH_3OH + 0.75\,SO_4^{2-} \longrightarrow HCO_3^- + 0.75\,HS^- + H_2O + 0.25\,H^+
\end{aligned}$$

22. The following reaction for dissolution of limestone by reaction with carbon dioxide and water is geochemically important.

$$CaCO_3(\text{calcite}) + H_2CO_3 \rightleftharpoons Ca^{2+} + 2\,HCO_3^-$$

    (a) Calculate the standard Gibbs energy change and the enthalpy change for the reaction at 25°C and 1 atm total pressure.
    (b) Calculate the equilibrium constant at 25°C and 1 atm total pressure.
    (c) Will an increase in temperature favor a shift toward products or reactants for this reaction?

23. Equilibrium constants are shown below for three reactions at 25°C. Use standard enthalpy data to prepare a plot showing $\log K$ as a function of temperature for the reactions over the range $5°\text{C} < T < 35°\text{C}$. Show all three curves on a single plot. For each reaction, is dissociation favored or disfavored by an increase in temperature?

$$\begin{aligned}
HCO_3^- &\rightleftharpoons CO_3^{2-} + H^+ &\qquad \log K &= -10.33 \\
NH_4^+ &\rightleftharpoons NH_3(aq) + H^+ &\qquad \log K &= -9.24 \\
H_2S(aq) &\rightleftharpoons HS^- + H^+ &\qquad \log K &= -7.02
\end{aligned}$$

24. Sketch plausible curves of $\overline{G}$, $\overline{H}$ and $T\overline{S}$ vs. reaction coordinate for each of the following scenarios. (Note: The information provided establishes certain

relationships that must be satisfied with respect to $\Delta\overline{G}_r$, $\Delta\overline{H}_r$, and $T\Delta\overline{S}_r$. The patterns of $\overline{G}$, $\overline{H}$, and $T\overline{S}$ in the transition from reactants to products are less well-defined, but nevertheless must meet certain constraints. Try to draw curves that are consistent with all of these considerations.)

(a) A reaction that is highly exothermic, approaches equilibrium very slowly, and can reach equilibrium by conversion of a small amount of reactants to products. Assume that the change in entropy favors the forward reaction, but the overall driving force for the reaction is dominated by the enthalpy change.

(b) A reaction that is slightly endothermic, approaches equilibrium rapidly, and requires conversion of a large amount of reactants to products to reach equilibrium.

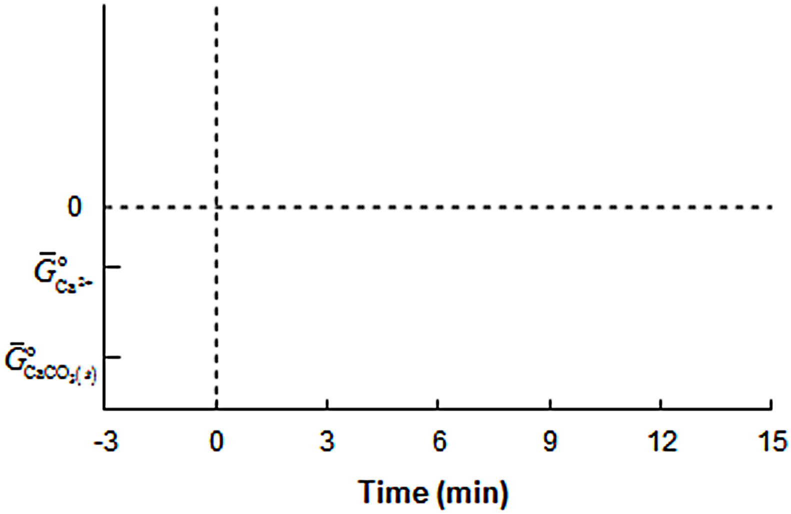
25. A solution at pH 8.8 and with an ionic strength is $0.003\,M$ contains $3.9 \times 10^{-5}\,M$ Ca^{2+}. The solution is in equilibrium with both the mineral calcite [$CaCO_3(s)$] and the $CO_2(g)$ in the atmosphere. NaCl is then added to increase the ionic strength to $0.2\,M$ while the pH is held constant. The calcite dissolution reaction is:

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad K = 10^{-8.30}$$

(Note: Thermodynamic data taken from different sources are often not entirely consistent. The value of K given here is based on the standard molar Gibbs energy values in Table 4.1. In later chapters, the equilibrium constant for the same reaction is given as $10^{-8.48}$ and is taken from a database associated with software for solving chemical equilibrium problems that is introduced in Chapter 7.)

(a) What is the reaction quotient, Q, for the $CaCO_3(s)$ dissolution reaction immediately after the salt addition, before any reaction has occurred?

(b) Eventually, the solution re-equilibrates with the solid and gas phases, at which point the activity of CO_3^{2-} is the same as it was before the salt addition. (The basis for this result is explained in Chapter 9.) On a copy of the following graph, sketch the profiles of $\overline{G}_{Ca^{2+}}$, $\overline{G}_{CaCO_3(s)}$ and $\Delta\overline{G}_r$ for the calcite dissolution reaction as a function of time, defining $t = 0$ as the time of salt addition. The sketch should go from a few minutes before the salt is added until 15 minutes after the salt addition, at which time the system is assumed to have reached equilibrium with both non-aqueous phases. Locations where $\overline{G}$ equals 0, $\overline{G}^{\circ}_{Ca^{2+}}$, and $\overline{G}^{\circ}_{CaCO_3(s)}$ are shown on the y-axis for reference.


0
$\bar{G}^\circ_{Ca^{2+}}$
$\bar{G}^\circ_{CaCO_3(s)}$
-3
0
3
6
9
12
15
Time (min)

CHAPTER 5 HOMEWORK PROBLEMS

In solving these problems, use K_a data from Table 5.1 and assume ideal solution behavior unless the question states otherwise or the ionic strength is given. If you prepare a $\log C$-pH diagram, label the axes and the individual curves, and include a caption. The range of values on the axes will depend on the details of the problem, but they should typically be 8 to 14 pH units on the abscissa and 6 to 10 log units on the ordinate.

1. How much HOCl must be added to pure water to make a solution of pH 4.3? pH 6.5? Do not assume $(\mathrm{H}^+) \gg (\mathrm{OH}^-)$ at pH 6.5.

2. Identify the strongest acid and the strongest base in the following reaction, using only the K value given.

$$\mathrm{H_2S + OCl^- \rightleftharpoons HOCl + HS^-} \qquad K = 10^{+0.51}$$

3. The bicarbonate ion concentration in a solution at pH 7.50 is $10^{-3.2}\,M$. Calculate the concentrations of all carbonate species and the total dissolved inorganic carbon (DIC) concentration in mol/L and g/L C.

4. A diprotic acid has $\mathrm{p}K_{a1} = 2.8$ and $\mathrm{p}K_{a2} = 8.4$. The standard Gibbs energy of formation of the most deprotonated species in this group (A^{2-}) is -85.2 kJ/mol. What is $\overline{G}^{\circ}_{\mathrm{H_2A}}$?

5. The transfer of a proton from butyric acid (stomach acid) to acetate can be described by the following reaction:

$$\mathrm{CH_3CH_2CH_2COOH + CH_3COO^- \rightleftharpoons CH_3CH_2CH_2COO^- + CH_3COOH}$$

$$\text{Butyric acid} + \text{Acetate} \rightleftharpoons \text{Butyrate} + \text{Acetic acid}$$

   (a) The equilibrium constant for this reaction is $K = 0.87$, and K_a for acetic acid is 1.74×10^{-5}. Using those values and K_w, compute the acid dissociation constant for butyric acid.

   (b) Write the reaction and determine the value of K_b (the basicity constant) for butyrate.

   (c) A solution is made by adding some acetic acid and some sodium butyrate to water. List all the species in the equilibrium solution that can act as acids, and rank them from most acidic to least acidic. Do the same for all species that can act as bases.

6. Dissolved copper ion (Cu^{2+}) can bond to several different molecules in aqueous solution, including some weak bases. Following are some of the reactions in which Cu^{2+} participates.

$$\begin{aligned}
&Cu^{2+} + Cl^- \rightleftharpoons CuCl^+ && \log K = 0.30\\
&Cu^{2+} + 2\,Cl^- \rightleftharpoons CuCl_2^\circ && \log K = -0.26\\
&Cu^{2+} + CO_3^{2-} \rightleftharpoons CuCO_3^\circ && \log K = 6.77\\
&Cu^{2+} + OH^- \rightleftharpoons CuOH^+ && \log K = 6.50\\
&Cu^{2+} + NH_3 \rightleftharpoons Cu(NH_3)^{2+} && \log K = 4.02\\
&Cu^{2+} + 2\,NH_3 \rightleftharpoons Cu(NH_3)_2^{2+} && \log K = 7.40
\end{aligned}$$

(a) What is the equilibrium constant for the following reaction?

$$Cu(NH_3)^{2+} + NH_4^+ \rightleftharpoons Cu(NH_3)_2^{2+} + H^+$$

(b) List the species that would be present at equilibrium if $10^{-3}\,M$ $Cu(HCO_3)_2$ and $10^{-3.3}\,M$ NaCl were added to water, and write the equations required to solve for the equilibrium concentrations of all these species. Include numerical values in the equations, if they are known.

(c) What is K_b for the base $CuOH^+$?

7. Write the charge balance for the following solutions and list the equations that would have to be solved to determine the equilibrium solution composition.

   (a) $10^{-3}\,M$ benzoic acid
   (b) $10^{-3}\,M$ Na_2S
   (c) $10^{-3}\,M$ $(NH_4)_2CO_3$
   (d) $10^{-3}\,M$ $(NH_4)_2CO_3$ plus $5 \times 10^{-3}\,M$ $(NH_4)_3PO_4$ plus $10^{-3}\,M$ $CaCO_3$

8. Using algebraic techniques and/or a spreadsheet approach, determine the equilibrium pH of each solution in Problem 7.

9. Prepare a log C-pH diagram for each solution in Problem 7. Use a full sheet of paper for each plot, and show the ranges $1 \le \text{pH} \le 13$ and $-10 \le \log C \le -1$.

10. When $PbCl_2$ is added to water, it dissociates into Pb^{2+} and Cl^- ions, and the Pb^{2+} ions then participate in the following reactions:

$$\begin{aligned}
&Pb^{2+} + OH^- \rightleftharpoons PbOH^+ && \log K = 6.40\\
&Pb^{2+} + 2\,OH^- \rightleftharpoons Pb(OH)_2^\circ && \log K = 10.91
\end{aligned}$$

   (a) What are pK_{a1} and pK_{a2} for Pb^{2+}?
   (b) How much $PbCl_2$ must be added to water to yield a solution of pH 5.1?

11. Determine the values of K_{b1}, K_{b2}, and K_{b3} for sodium arsenate, Na_3AsO_4, and write the reactions to which these constants apply. Also determine K for the reaction in which arsenic acid (H_3AsO_4) completely dissociates to form arsenate ion (AsO_4^{3-}).

12. Na_2CO_3 is added to pure water until the pH is 9.45.
    (a) What is $TOT\text{CO}_3$ in the solution?
    (b) How much HCl would have to be added to the solution to lower the pH to 7.0?
    (c) How much H_2CO_3 would have to be added to the solution to lower the pH to 7.0?

13. Cyanide ion, CN^-, is important in metal plating industries because it can keep metals dissolved under conditions where they would otherwise form solids (precipitate) and settle out of solution. The details of how this occurs are presented in Chapter 11. It is important to maintain pH>10.5 in these solutions to minimize release of toxic hydrogen cyanide gas. If a solution is prepared by dissolving $10^{-2} M$ NaCN in water, will the pH be in the region where the solution is safe? What is the HCN concentration in the solution?

14. A solution containing $0.04\,M$ NaCl and $5 \times 10^{-4} M$ of a base NaX has a pH of 8.9. Estimate K_a of the acid HA, taking nonideal solute behavior into account. Hint: There are many approaches for solving the set of equations that characterize this problem. One approach is to guess the ionic strength of the solution, solve the remaining equations based on that guess, and determine a new value for the ionic strength based on the computed composition. Then, revise the original guess to equal the computed ionic strength and repeat the process until the guessed and computed values converge.

15. A solution contains $10^{-4} M$ $TOT\text{OCl}$, 90% of which is present as HOCl. The solution also contains $7 \times 10^{-4} M$ H_2CO_3. What is $TOT\text{CO}_3$ in the solution?

16. Uncharged ammonia [$NH_3(aq)$] is toxic to fish at a concentration of 0.01 mg/L $NH_3{-}N$. What is the maximum concentration (mg/L) of total ammonia nitrogen (the sum of the N concentrations in NH_3 and NH_4^+) that can be in solution without causing toxicity at pH 7.0? At pH 9.0?

17. You wish to add enough NaOCl (sodium hypochlorite) to a 150-m^3 (~400,000-gal) swimming pool to provide a dose of 5.0 mg/L $TOT\text{OCl}$ *as Cl_2*.
    (a) How much NaOCl (kg) should you add? The EW of NaOCl is based on the reaction: $NaOCl + 2\,H^+ + 2\,e^- \rightleftharpoons Na^+ + Cl^- + H_2O$.

(b) The pH in the pool after adding the NaOCl is 8.67. To improve disinfection, you want at least 90% of the TOTOCl to be in the form of HOCl. Assuming that HOCl/OCl^- is the only weak acid/base group in the solution, what volume (L) of $10N$ HCl must be added to the stock solution to achieve the goal?

18. Several simple acids and bases are common constituents of household items. Among these are acetic acid (vinegar), bicarbonate of soda ($NaHCO_3$), ammonia, ascorbic acid (vitamin C [$C_6H_8O_6$], a diprotic acid with $pK_{a1} = 4.10$ and $pK_{a2} = 12.35$), sodium hypochlorite (bleach), and trisodium phosphate (in many cleansers).

    (a) A six-year-old playing chemist finds some of these items in a cupboard and decides to mix some vinegar, vitamin C, bleach, and cleanser, hoping to make something exciting happen (like an explosion, or at the very least some serious fizzing). Alas, nothing dramatic occurs, and she decides to devote her energy to theory rather than experimentation. Hence, she decides to list:

    (i) all the chemical species that she thinks were in the mixture;
    (ii) the species that could act as acids and those that could act as bases, listing each from weakest acid to strongest (including the acid/base reactions of H_2O); and
    (iii) the equations necessary to solve for the solution pH.

    Being rather precocious, she does this perfectly. Reproduce the lists that she prepared.

    (b) Having opened the bottle of ammonia, she finds the odor offensive and decides to eliminate it. The odor, she knows, is from evaporation of NH_3°, because ammonium ions (NH_4^+) cannot enter the gas phase in significant concentrations. Having already used most of the other 'reagents' available to her, she has only bicarbonate of soda, vinegar, and some cleanser containing trisodium phosphate remaining. Which should she add? Explain briefly.

19. What is the pH of a solution made by adding $10^{-2}M$ sodium benzoate (C_6H_5COONa) to pure water, taking into account nonideal solute behavior? Benzoate is the conjugate base of benzoic acid, a common preservative added to food and beverages. It might be useful to see the Hint in Problem 14.

20. What is the composition of a solution made by adding $0.01M$ $Ca(OCl)_2$ to pure water, assuming ideal behavior? How much would the computed concentration of OCl^- change if nonideal solute behavior were taken into account? It might be useful to see the Hint in Problem 14.

21. The concentration of ammonia in a gas phase $[\mathrm{NH_3}(g)]$ that is in equilibrium with a solution depends on the dissolved concentration of $\mathrm{NH_3}(aq)$ but is independent of the dissolved $\mathrm{NH_4^+}$ concentration.

    (a) Calculate pH and $\mathrm{NH_3}(aq)$ in solutions made by adding 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}, and $1.0\,M$ $\mathrm{NH_3}$ to pure water. Assume ideal solution behavior in all cases. Plot pH and the $\mathrm{NH_3}(aq)$ concentration vs. the logarithm of the dose of $\mathrm{NH_3}$ added. Why is the $\mathrm{NH_3}(aq)$ concentration not proportional to the amount of ammonia added ($TOT\mathrm{NH_3}$)?

    (b) Carry out similar calculations as in part (a) for the same concentrations of $TOT\mathrm{NH_3}$ added, but in this case calculate the pH and concentration of $\mathrm{NH_4^+}$ when $\mathrm{NH_4Cl}$ is added to the solution. In this case, the concentration of $\mathrm{NH_4^+}$ is (almost) proportional to $TOT\mathrm{NH_3}$ added. Why?

22. Would the acidity constant, K_a, for the $\mathrm{NH_4^+}/\mathrm{NH_3}(aq)$ acid/base pair increase, decrease, or remain the same if the reference state environment were changed from infinite dilution in pure water to infinite dilution in major-ion seawater? Explain your reasoning.

23. An acid $\mathrm{H_2A}$ is stable in solution in both the fully protonated ($\mathrm{H_2A}$) and the fully deprotonated $(\mathrm{A^{2-}})$ forms, but the intermediate species ($\mathrm{HA^-}$) is negligibly stable and is never present at a significant concentration.

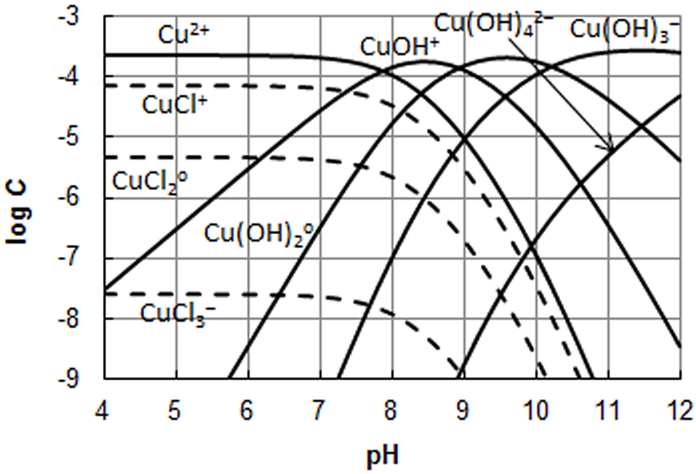
    (a) A solution of $3 \times 10^{-3}\,M$ $\mathrm{H_2A}$ has a pH of 3.7. Find the product $K_{a1}K_{a2}$, assuming ideal solute behavior.

    (b) What are the pH and composition of a solution prepared by adding $0.05\,M$ $\mathrm{CaCl_2}$, $3 \times 10^{-4}\,M$ $\mathrm{Na_2A}$ and $3 \times 10^{-4}\,M$ NaHA to water? (Even though $\mathrm{HA^-}$ is unstable in water, it can be present in a dry salt that can be added to a solution.) Ignore the acid/base reactions of $\mathrm{Ca^{2+}}$, and assume that Davies equation applies. When computing activity coefficients, note that $TOT\mathrm{Ca}$ and $TOT\mathrm{Cl}$ are much greater than $TOT\mathrm{A}$.

24. The log C-pH diagram shown below shows the speciation of $\mathrm{Cu^{2+}}$ in a solution containing $3 \times 10^{-4}\,M$ $TOT\mathrm{Cu}$ and with the $\mathrm{Cl^-}$ concentration and ionic strength of seawater ($\sim 0.5\,M$, and $\sim 0.7\,M$, respectively). (Some polymeric species have been excluded from the calculations.) Activity coefficients were determined with the Davies equation. Using only information from the graph and K_w, determine the following equilibrium constants:

    (a) K_b for the dissolved base $\mathrm{Cu(OH)_2^\circ}$.

    (b) K_{eq} for the reaction: $\mathrm{Cu^{2+}} + 2\,\mathrm{Cl^-} \rightleftharpoons \mathrm{CuCl_2^\circ}$.



25. As indicated in Table 5.1, citric acid (which we can abbreviate as H_3Cit) is a triprotic carboxylic acid.

    (a) A solution is made by adding lemon juice to water until the pH is 2.20. Assuming all the acidity is from dissociation of citric acid, find the total concentration of citrate species (i.e., TOTCit) and the concentration of $HCit^{2-}$.

    (b) The solution in part (a) is diluted 1 : 10 and partly neutralized by addition of sodium bicarbonate ($NaHCO_3$). Designating the total concentration of carbonate species added as $TOTCO_3$, write all the equations necessary to compute the new pH. You need not solve the equations.

    (c) If the final pH is 6.0, what is the ratio of (HCO_3^-) to (H_2CO_3) in the solution? What is the ratio of (CO_3^{2-}) to (H_2CO_3)? Would these ratios change if the pH were still 6.0, but TOTCit were doubled?

26. A brine with an ionic strength of $0.1\,M$ is at pH 8.8 and contains 2.2 mg/L TOTZn.

    (a) Determine the $K_{a,\text{eff}}$ values for formation of $Zn(OH)_x^{2-x}$ species for $1 \leq x \leq 4$.

    (b) What are the concentrations and activities of Zn^{2+} and $Zn(OH)_2^o$ in the solution?

27. One hundred micromoles (10^{-4} moles) of solid calcium phosphate ($Ca_3(PO_4)_2(s)$) is added to 1.0 L of pure water. When the solution reaches equilibrium, the pH is 9.34.

    (a) Explain why the pH increased above that of the pure water (7.0).

(b) Write the equations that would have to be solved to determine the equilibrium pH if the system had not been investigated experimentally. Assume that the solution behaves ideally.

(c) When the system reaches equilibrium, the concentrations of total dissolved Ca ($TOT\text{Ca}$) and total dissolved phosphate ($TOT\text{PO}_4$) are $3.34 \times 10^{-5}\,M$ and $2.23 \times 10^{-5}\,M$, respectively. If an additional 1.0 L of pure water is added to the suspension, and the system then re-equilibrates, will the pH increase, decrease, or remain the same as before the water was added? Explain briefly.

CHAPTER 6 HOMEWORK PROBLEMS

In solving these problems, use K_a data from Table 5.1 and assume ideal solution behavior unless the question states otherwise or the ionic strength is given. If you prepare a log C-pH diagram, label the axes and the individual curves, and include a caption. The range of values on the axes will depend on the details of the problem, but they should typically be 8 to 14 pH units on the abscissa and 6 to 10 log units on the ordinate.

1. Using a graphical approach, solve for the pH of the following solutions.

(a) $10^{-3}\,M$ HAc	(e) $10^{-3}\,M$ HCN
(b) $10^{-3}\,M$ HOCl	(f) $10^{-3}\,M$ Na_2CO_3
(c) $10^{-3}\,M$ NaCN	(g) $10^{-3}\,M$ $NaHCO_3$
(d) $10^{-3}\,M$ Na_2Oxalate	(h) $10^{-3}\,M$ $(NH_4)_2CO_3$

2. Prepare a log C-pH diagram for a solution containing $10^{-4}\,M$ chromic acid (H_2CrO_4). Indicate the values of the slopes of the lines on the diagram. What is the predominant species of chromium in this solution, and what is its concentration, at pH 6? at pH 8?

3. What are the concentrations of all species in a solution of $10^{-2}\,M$ Na_2CO_3? $10^{-2}\,M$ $NaHCO_3$? $10^{-2}\,M$ H_2CO_3?

4. Identify the dominant species and prepare a tableau using those species as components for the solutions described below. Prepare a log C-pH diagram and determine the equilibrium pH and the concentrations of all species in each system.

   (a) $10^{-3}\,M$ $NaHCO_3$ $+10^{-2}\,M$ HCl $+10^{-2}\,M$ NaOH
   (b) $10^{-3}\,M$ $NaHCO_3$ $+10^{-3}\,M$ HCl $+10^{-2}\,M$ NaOH
   (c) $10^{-3}\,M$ $NaHCO_3$ $+10^{-2}\,M$ HCl $+10^{-3}\,M$ NaOH

5. Write the TOTH equation for each of the following systems, using the dominant species as components.

   (a) $0.02\,M$ HCl
   (b) $10^{-3}\,M$ NaCN
   (c) $10^{-3}\,M$ HOCl
   (d) $10^{-4}\,M$ $NaHCO_3$ $+10^{-4}\,M$ NH_4Cl
   (e) $10^{-3}\,M$ NaCN $+10^{-3}\,M$ HOCl

6. Write the TOTH equation for the following systems.

   (a) $10^{-3}\,M$ Na_3PO_4 $+10^{-4}\,M$ Na_2HPO_4 + H_2O, using PO_4^{3-} as a component.

(b) Same system as (a), using HPO_4^{2-} as a component.

(c) $10^{-3}\,M$ NH_4Cl $+5 \times 10^{-3}\,M$ HNO_3 $+2 \times 10^{-3}\,M$ NaOH $+H_2O$, using dominant species as components.

7. The effluent from an anaerobic digester is simulated as a mixture of $5 \times 10^{-4}\,M$ each of NaH_2PO_4 and Na_2HPO_4, and $6 \times 10^{-4}\,M$ each of NH_3, H_2CO_3, and $NaHCO_3$.

   (a) Identify the species that you think will be dominant in each acid/base group in the equilibrated solution.

   (b) Write the *TOT*H equation for the system, using H_2O, H^+, $H_2PO_4^-$, NH_3, HCO_3^-, and Na^+ as components.

   (c) Estimate the equilibrium pH, assuming ideal solute behavior. (You can sketch a log *C*-pH diagram if you'd like, but you need not do so to answer the question.)

8. The organic chemical ethylene diamine tetra-acetate ($EDTA^{4-}$) is used extensively in industrial processes to prevent metals from precipitating as solids. The pK_{ai} values for H_4EDTA are 2.11, 3.12, 6.27, and 10.95 for *i* equal to 1 through 4, respectively.

   (a) At what pH or over what pH range is the activity of $HEDTA^{3-}$ greater than that of H_4EDTA?

   (b) Write the expression and compute the value of K_b for the reaction in which H_3EDTA^- serves as the conjugate acid.

   (c) Prepare a log *C*-pH diagram for a solution of $3 \times 10^{-3}\,M$ *TOT*EDTA. What is the slope of the curve for H_4EDTA at $pH = pK_{a3}$?

   (d) A solution of $1 \times 10^{-3}\,M$ Na_2H_2EDTA and $2 \times 10^{-3}\,M$ Na_3HEDTA is prepared. Develop the tableau for the solution using the EDTA species that you expect to be dominant as a component. Write the *TOT*H equation, and determine the speciation of EDTA at equilibrium.

9. A solution is made by adding 2×10^{-4} moles of oxalic acid (which we will represent as H_2Ox), 5×10^{-4} moles Na_2HPO_4, and 5×10^{-4} moles $CuCl_2$ to 1.0 L of pure water.

   (a) Prepare a log *C*-pH diagram showing the speciation of *TOT*Ox, *TOT*PO_4, and *TOT*Cu in the system.

   (b) H_3PO_4 is added to the original solution until the pH is 5.5. Designating the dose of H_3PO_4 added (in mol/L) as *x*, write out the *TOT*H equation for the solution, using the species that are expected to be dominant in the new solution as the components.

10. A wastewater from an electroplating process is at pH 2.5, due primarily to the presence of nitric acid, HNO_3, with $pK_a = -1.5$. The solution contains $6 \times 10^{-4} M$ *TOT*Cu, almost all of which is present as Cu^{2+}. The wastewater is to be neutralized using a solution that was originally prepared as $0.2 M$ NaOH. However, the NaOH solution has been exposed to the atmosphere for some time, and CO_2 has dissolved into it, so that *TOT*CO_3 is now $0.02 M$.

    (a) Prepare a log C-pH diagram for a solution containing $0.02 M$ *TOT*CO_3 and use it to determine the pH of the NaOH solution after the CO_2 dissolves.

    (b) Add curves to the log C-pH diagram for Cu^{2+} and $Cu(OH)_x^{2-x}$ species for $x \leq 4$. Write a *TOT*H equation for the waste solution after 30 mL of the alkaline, neutralizing solution has been added per liter of wastewater. Because the volume of titrant added is only 3% of the volume of wastewater solution, dilution of the wastewater can be ignored. What is the pH of the mixture?

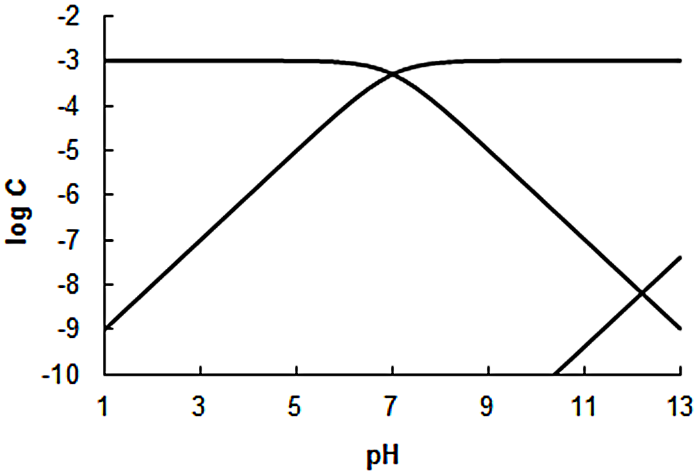
11. A log C-pH diagram for a solution containing $10^{-3} M$ hydrogen sulfide (H_2S) is provided below.

    (a) Label the lines with the species they represent and assign correct values to the axes.

    (b) Draw lines for H^+ and OH^- on the diagram.

    (c) What is the pH of a solution of $10^{-4} M$ NaHS plus $9 \times 10^{-4} M$ H_2S?

    (d) Would a solution of $0.5 \times 10^{-4} M$ Na_2S plus $9.5 \times 10^{-4} M$ H_2S be more acidic, more alkaline, or the same as the solution in part (c)? Explain your answer in one or two sentences or equations.



12. Consider an acid H_2A with $pK_{a1} = 5.5$ and $pK_{a2} = 9.5$, in a solution with $10^{-2}\,M\ TOT\mathrm{A}$.

   (a) At what pH or in what pH range (if any) will the following conditions be met?

      (i) The concentration of A^{2-} increases by approximately a factor of 100 for every increase of one pH unit?

      (ii) The concentration of HA^- decreases by approximately a factor of 10 for every increase of one pH unit?

      (iii) The concentration of H_2A increases by approximately a factor of 10 for every increase of one pH unit?

      (iv) The ratio $(H_2A)/(A^{2-})$ decreases by approximately a factor of 100 for every increase of one pH unit?

      (v) The value of $p(HA^-)$ is approximately 2.3?

      (vi) The value of $p(H_2A)$ is approximately 4.0?

   (b) What is the pH of a solution of $0.005\,M\ H_2A + 0.005\,M$ NaHA?

   (c) Write the TOTH equation and determine the pH of a solution of $5 \times 10^{-3}\,M\ Na_2A + 5 \times 10^{-3}\,M\ H_2A$.

   (d) Will a solution of $10^{-2}\,M$ NaHA be acidic, neutral, or alkaline?

   (e) Write the equilibrium equation and the form and the value of K_b for HA^-, i.e., HA^- acting as a base.

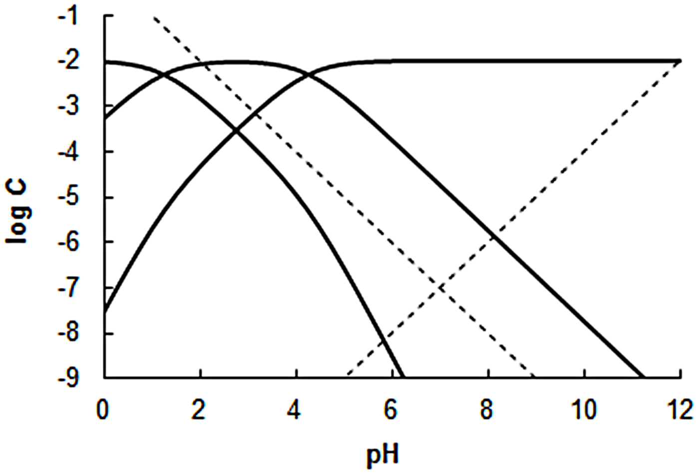
13. The following figure is a log C-pH diagram for oxalic acid.

   (a) What is TOTOx? What are pK_{a1} and pK_{a2}?

   (b) Over what range of pH values is HOx^- the predominant oxalate species?

   (c) Is H_2Ox a relatively strong or weak acid?

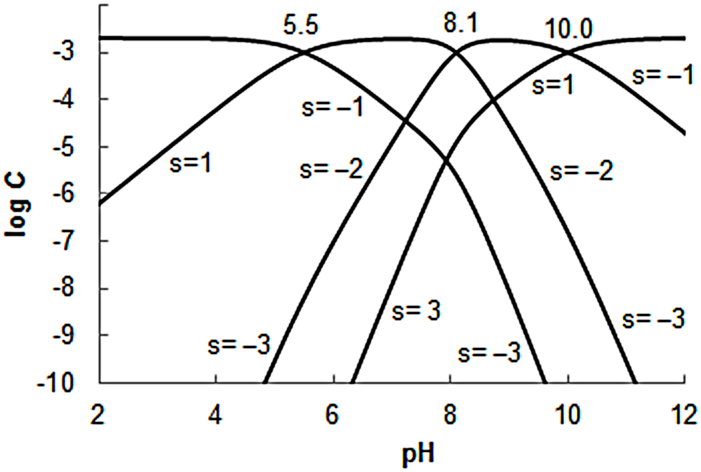
   (d) If $10^{-2}\,M$ NaHOx were added to water, what would the solution pH be?



14. A log C-pH diagram for an acid/base system containing $10^{-2.7}$ M TOTA is shown below. The fully protonated form of the acid is H_4A. However, the curves are shown for only three species, because one of the potential H_nA^{4-n} species is so unstable that its concentration in this system is always less than 10^{-10} M. The 's' values indicate the approximate slopes of the curves in the given region, and the pH values indicate the intersection points of the various curves.

   (a) What is the equilibrium constant for the reaction $H_3A \rightleftharpoons HA + 2\,H^+$?

   (b) What is the value of K_b for a reaction in which HA is the acid?



15. Nickel can combine sequentially with three OH⁻ ions to form 'nickel hydroxo complexes' via the following reactions.

$$Ni^{2+} + OH^- \rightleftharpoons NiOH^- \qquad \log K = 4.60$$

$$Ni^{2+} + 2\,OH^- \rightleftharpoons Ni(OH)_2^\circ \qquad \log K = 8.96$$

$$Ni^{2+} + 3\,OH^- \rightleftharpoons Ni(OH)_3^- \qquad \log K = 11.98$$

   (a) Combine these reactions with K_w so that they have the form of K_a's. Determine which species is dominant at any given pH in the range from 0 to 14.

   (b) Prepare a log C-pH diagram for a solution containing 10^{-2} M TOTNi in the pH range 6 to 13 and for log C values from -2 to -8. (Hint: the diagram might be difficult to draw at first, because the acidity of various nickel species is unusual in a way that will be apparent from the K_a values. Despite the unusual features, the diagram must reflect the basic equations that characterize any acid/base system: the mass balances and equilibrium constants. On the other hand, there is nothing fundamental about the "look" of graphs that you have become accustomed to. If you are having difficulty drawing the graph, use a spreadsheet to compute the α values of the different species over a range of pH values, and plot the results. Once you have drawn the graph, you will be able to see how and, hopefully, why the appearance of this graph is slightly different from that of most log C-pH diagrams you have seen previously.)

  (c) What is the pH of a solution of $10^{-2}\,M$ $\mathrm{Ni(NO_3)_2}$?

16. Chromic acid ($\mathrm{H_2CrO_4}$) is a diprotic acid which has important uses in industrial processes and in preparation and analysis of environmental samples. Under certain conditions it can "dimerize" according to the following reaction:

$$2\,\mathrm{HCrO^-} \rightleftharpoons \mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O} \qquad \log K = 1.54$$

The product shown is called dichromate ion and is the deprotonated form of a strong diprotic acid. The acidity constants for chromate are $\mathrm{p}K_{a1} = 0.20$ and $\mathrm{p}K_{a2} = 6.51$, and those for dichromate are $\mathrm{p}K_{a1} < 0$; $\mathrm{p}K_{a2} = -0.07$. Find the pH and composition of the following two solutions:

  (a) $0.2\,M$ $\mathrm{Na_2CrO_4 + H_2O}$
  (b) $0.2\,M$ $\mathrm{NaHCrO_4 + H_2O}$

(Hint: Because of the dimerization reaction, the total molar concentration of dichromate species in a system where most of the Cr is dimerized is different from the total molar concentration of chromate in the system when most of the Cr is present as the monomer. Write out the mass balance and equilibrium equations as the first step in your analysis. Then either solve those equations or develop a log C-pH diagram by substituting into the mass balance on Cr until it contains $\mathrm{H^+}$ and one Cr containing species as the only variables. You can then solve that equation at various pH values and use the results to determine the concentrations of the other Cr containing species, so that the complete diagram can be drawn. Note that only one Cr-containing species can be chosen arbitrarily as a component for the TOTH equation.)

17. Citric acid is triprotic ($\mathrm{H_3Cit}$), with acidity constants $\mathrm{p}K_{a1} = 3.13$, $\mathrm{p}K_{a2} = 4.76$, and $\mathrm{p}K_{a3} = 6.40$.

  (a) Write out the expressions for α_0, α_1, α_2, and α_3 as a function of the K_a values and $(\mathrm{H^+})$.
  (b) Identify the region where each citrate species is dominant.
  (c) Determine which terms in the denominators for the α values are significant at pH 7.5 (terms contributing less than 5% to the summation can be considered negligible). For a solution with $10^{-1}\,M$ total citrate, write out an

approximate equation of the form: [$\log C = \text{constant} + n\text{pH}$] for each citrate species at pH 7.5, approximating the dominant species' concentration as TOTCit.

(d) Draw a log C-pH diagram for a solution with $10^{-1}\,M$ TOTCit over the pH range $1.0 < \text{pH} < 8.0$.

(e) Find the pH of the following solutions:

  (i) $10^{-1}\,M$ H_3Cit + water
  (ii) $10^{-1}\,M$ Na_2HCit + water
  (iii) $0.05\,M$ $Na_3Cit + 0.05\,M NaH_2Cit$ + water

18. A wastewater is simulated as an ideal solution containing $10^{-2.7}$ M $NaHCO_3$ and 10^{-3} M NH_4Cl.

  (a) Prepare a log C-pH diagram for the system.
  (b) Predict the dominant species in the equilibrium solution, and prepare a system tableau using those species as components.
  (c) Write the TOTH equation and use it to determine the pH of the solution.
  (d) The utility hopes to remove nitrogen from the solution by driving out NH_3 gas. To prepare for that step, 148 mg/L $Ca(OH)_2$ (hydrated lime) will be added to raise the pH and convert NH_4^+ to $NH_3(aq)$. Calculate the pH after lime addition, but before any NH_3 exits the solution.

19. Acid drainage from coal mines can make the receiving waters uninhabitable by fish. To remediate one such situation, a consultant has recommended dissolving limestone, $CaCO_3$, in the drainage water to neutralize the acid. The pH of the untreated water is 2.40 due to the following overall reaction:

$$FeS(s) + 2.25\,O_2(aq) + 2.5\,H_2O \longrightarrow Fe(OH)_3(s) + SO_4^{2-} + 2\,H^+$$

(Note: This reaction is shown only to illustrate how the SO_4^{2-} and H^+ enter the water. The following questions focus just on the concentrations of these ions in solution; you need not consider the other chemicals in the reaction when answering the questions.)

  (a) Determine the concentration of $TOT SO_4$ in the drainage water using manual calculations. Use the Davies equation to model activity coefficients. Is HSO_4^- a strong acid in this solution? (Hint: write out the mathematical expressions that relate the concentrations of H^+, HSO_4^-, and SO_4^{2-} to known values and/or each other. Some of these relationships will include activity coefficients. Then, make a guess for the ionic strength of the solution, compute the activity coefficients, and solve for the species concentrations. Finally, test whether the ionic strength based on those concentrations is consistent with your guess. If not, iterate on the guess until it converges with the computed value.)

(b) Prepare the system tableau for the solution after it has been neutralized to pH 7.0 by addition of $CaCO_3$, and write the corresponding TOTH equation. Use the expected dominant species as components.

(c) What is TOTCa in the stream after the pH has been raised to 7.0? As in part (a), use the Davies equation to estimate activity coefficients.

CHAPTER 7 HOMEWORK PROBLEMS

1. The easiest, and perhaps only, way to familiarize yourself with the capabilities and limitations of Visual Minteq or similar software is to use it. Numerous acid/base example problems have been solved using manual or spreadsheet approaches in Chapters 5 an 6, and many other problems without solutions are provided at the ends of those chapters. Solve or re-solve some of those problems using Visual Minteq, practicing all techniques introduced in this chapter (e.g., drawing $\log C{-}$pH diagrams, exploring the effects of ionic strength on speciation, and defining new components and species that are not in the Visual Minteq data base). In each case, compare the results of the calculations using the different methods and try to understand the basis of any differences. Your instructor may specify some problems for you to hand in, but it will behoove you to go beyond those assignments to become as proficient as possible at using the program.

   In presenting the results of your simulations, you should provide an explanation of how the problem was set up and solved with the program, give the results in a well formatted and titled table, and include appropriate axis labels and a caption for all graphs. Program output can be appended to your solution, but it is not acceptable to turn in only raw computer output.

   Note that Visual Minteq reports results for all species considered, even if they are present at absurdly low concentrations. When presenting your results, show only data that is relevant to the question. Although some exceptions exist, this guideline means that the lowest value of $\log C$ on your plots should typically be in the range of -8 to -12.

CHAPTER 8 HOMEWORK PROBLEMS

Note: Many of the following problems can be solved either manually or using software like Visual Minteq. Your instructor will indicate whether you should use a particular approach, or whether the choice is up to you. In some cases, a manual solution is a practical option only if some simplifications are made (e.g., ignoring some of the species that might form). Again, your instructor will provide guidance on this issue. If chemical equilibrium software is used, present your solution with an explanation of how the problem was set up and solved with the program, give the results in a well formatted and titled table, and include appropriate axis labels and a caption for all graphs. Program output can be appended to your solution, but it is not acceptable to turn in only raw computer output. In all cases, assume ideal behavior unless the ionic strength is given explicitly or is to be computed as part of the problem.

1. The following solutions have been prepared:

   Solution 1: H_2O plus sufficient NaOH to adjust the pH to 8.0.
   Solution 2: $10^{-3} M\ TOT$OCl plus sufficient HCl and/or NaOH to adjust the pH to 8.0.
   Solution 3: $10^{-2} M\ TOT$OCl plus sufficient HCl and/or NaOH to adjust the pH to 8.0.

   (a) In Solutions 2 and 3, one-half of the TOTOCl was added as HOCl and one-half as NaOCl. Find the amount of HCl or NaOH that was needed to adjust the pH to 8.0 in each solution.

   (b) Compute and compare the pH when 10^{-3} moles of HCl is added to 1 L of each of the three solution.

2. Plot a log C-pH diagram for a system containing $10^{-2} M\ TOT\text{PO}_4$. Prepare a table showing the pH and the concentration of all phosphate species for HCl additions of 0, 5, 10, 15, 20, 25 and 30 meq/L to a solution of $10^{-2} M$ Na_3PO_4.

3. A solution of $0.1 N$ (i.e., 0.1 equiv/L) NaOH is added to 70 mL of $0.1 M$ HAc. What will the solution pH be after addition of (a) 35, (b) 70, and (c) 105 mL of the titrant? Assume ideal solution behavior, and take into account the dilution of the original solution by the titrant.

4. A solution contains $10^{-2.8} M\ TOT\text{CO}_3$ and is at pH 8.1.

   (a) Calculate and plot a titration curve for incremental additions of HCl until the pH is lowered to 4.0.

   (b) How much HCl (moles per liter of solution) is required to titrate the solution to pH 7.0? to the CO_2 equivalence point?

5. A solution contains only one acid/base group, HA/A^-, at a total concentration of $2 \times 10^{-4}\,M$. pK_a for HA is 9.0. If the solution is titrated from pH 9.0 to 10.0, what fraction of the NaOH added is attributable to reactions of the TOTA? Put another way, what is the ratio of the amount of base is needed to carry out the titration with the HA/A^- species present to the amount that would be required if they were absent?

6. A water sample at pH 6.5 has been titrated with both strong acid (HCl) and strong base (NaOH). The amount of titrant added at increments of 0.2 pH unit is summarized below, where the values represent the cumulative acid or base addition at each pH value. The sample is thought to contain just one or two weak acid/base groups. Analyze the titration curve to determine the number of acid/base groups present and the total concentration and pK_a of each group. Hint: try to isolate the effect of the weak acid/base groups by separating their contribution to the overall curve from the contribution needed just to titrate pure water.

pH	Base (meq/L)	pH	Base (meq/L)	pH	Acid (meq/L)	pH	Acid (meq/L)
6.5	0.000	8.9	0.028	6.5	0.000	4.7	0.327
6.7	0.004	9.1	0.038	6.3	0.006	4.5	0.409
6.9	0.006	9.3	0.054	6.1	0.015	4.3	0.493
7.1	0.008	9.5	0.079	5.9	0.028	4.1	0.576
7.3	0.009	9.7	0.119	5.7	0.049	3.9	0.661
7.5	0.010	9.9	0.175	5.5	0.080	3.7	0.766
7.7	0.011	10.1	0.262	5.3	0.122	3.5	0.901
7.9	0.012	10.3	0.390	5.1	0.177	3.3	1.10
8.1	0.013	10.5	0.571	4.9	0.246	3.1	1.39
8.3	0.014	10.7	0.820				
8.5	0.017	10.9	1.19				
8.7	0.021	11.1	1.72				

7. Calculate the initial pH and the pH at both equivalence points for titration of $10^{-2}\,M$ Na_2CO_3 with strong acid. Next, based on your qualitative understanding of titrations, sketch the titration curve and buffer intensity curve for such a titration. Finally, use a spreadsheet or Visual Minteq to determine the two curves accurately. Compare your sketches to the calculated curves and describe the reasons that led to the discrepancies in your sketches.

8. Colorimetric indicators are convenient for evaluating the pH of a solution to within a few tenths of a unit. They are also very useful for indicating the endpoint of a titration. Consider a model indicator "In" which can exist as H_2In^+, HIn°, or In^-, with p$K_{a1} = 6.0$ and p$K_{a2} = 9.0$. H_2In^+ is red, HIn° is colorless, and In^- is blue, with the red or blue color becoming noticeable when

the solution contains at least $10^{-7}\,M$ of the respective species.

(a) What are the pH and color of a solution made by adding $5 \times 10^{-7}\,M$ H_2InCl to water?

(b) A solution contains $10^{-3}\,M$ ammonium carbonate, $(NH_4)_2CO_3$, and $5 \times 10^{-4}\,M$ lime, $Ca(OH)_2$. Then, $5 \times 10^{-7}\,M$ H_2InCl is added. What are the color and pH of the system?

(c) Nitric acid (HNO_3) is added to the solution in part (b) until the solution turns red. What is the pH? How much nitric acid was added?

(d) If the solution in part (b) were adjusted to pH 12.0 with strong base and were then titrated with HNO_3 to pH 4.0, would the blue-to-colorless or colorless-to-red change be sharper? That is, which would occur over a smaller range of acid added? Why? Assume that both color changes occur over a pH range of about 0.1 pH unit.

9. (a) How much does the alkalinity of a water sample change upon addition of $10^{-4}\,M$ of the following chemicals? Assume alkalinity is determined by titration to pH 4.5, that the solutions are ideal, and that the water is initially at pH 7.5 due to the presence of an unknown mixture of weak acids and bases. Briefly explain your reasoning.

   (i) HCl
   (ii) NaOH
   (iii) Na_2CO_3
   (iv) $NaHCO_3$
   (v) CO_2
   (vi) NaH_2Cit
   (vii) $FeCl_3$

   (b) How would your answers to part (a) be different if the solutions were initially at pH 8.5? You need not do any calculations; just explain the reasoning that leads you to conclude whether the change in the alkalinity would be larger, smaller, or the same.

10. You have prepared a solution by adding enough Na_2CO_3 to 2 L of deionized water to provide an alkalinity of 160 mg/L *as $CaCO_3$*. However, you subsequently find out that that bottle had previously contained $4\,M$ HAc, and you are not sure that it was thoroughly cleaned before you used it. You measure the pH of your solution and find that it is 10.1. Determine whether any HAc was left in the bottle when you began your efforts and, if so, estimate its volume.

11. You wish to make a solution that has an alkalinity of 1.5 meq/L, with equal portions of the alkalinity contributed by NaOH, $NaHCO_3$, and Na_2CO_3. How much of each chemical should you add, in mg/L?

12. A solution at pH 8.0 contains $10^{-3}\,M$ TOTAc and has an alkalinity of 1.5 meq/L. If the non-acetate alkalinity is contributed by carbonate species, what is $TOT\mathrm{CO_3}$?

13. A water contains $10^{-3}\,M$ $\mathrm{Na_2CO_3}$ and $10^{-3}\,M$ HCl. What is the alkalinity in equiv/L and mg/L *as* $CaCO_3$?

14. Estimate the alkalinity of a solution containing the following major species, based on titration with HCl to an endpoint of pH 4.5. Use the Davies equation to estimate activity coefficients.

$TOT\mathrm{Na} = 2 \times 10^{-3}\,M$ $\qquad$ $TOT\mathrm{CO_3} = 2 \times 10^{-3}\,M$

$TOT\mathrm{Ca} = 2 \times 10^{-3}\,M$ $\qquad$ $TOT\mathrm{PO_4} = 2 \times 10^{-3}\,M$

$\mathrm{pH} = 7.2$ $\qquad$ $TOT\mathrm{Cl} = 1 \times 10^{-3}\,M$

15. Calculate the alkalinity of aqueous solutions with the following characteristics:
    (a) pH= 3.5, $TOT\mathrm{CO_3} = 10^{-3}\,M$
    (b) pH= 7.5, $TOT\mathrm{CO_3} = 10^{-3}\,M$
    (c) pH= 11.5, $TOT\mathrm{CO_3} = 10^{-3}\,M$

16. An organic acid has been added to a solution with an alkalinity of 50 mg/L *as* $CaCO_3$. The alkalinity was added entirely as NaOH. If the total concentration of the organic acid added was $10^{-2.9}\,M$ and the final pH was 5.2, what is pK_a of the acid?

17. An ideal solution has an alkalinity of 120 mg/L *as* $CaCO_3$. One-fourth of the alkalinity is provided by hydroxide ions, and the rest by carbonate species. Determine the pH of the solution and $TOT\mathrm{CO_3}$.

18. An anaerobic biological treatment process is being designed to treat a solution containing 4000 mg/L HAc. The bacteria can convert acetic acid to carbon dioxide and methane by the following reactions, but only if the pH is above 5.2.

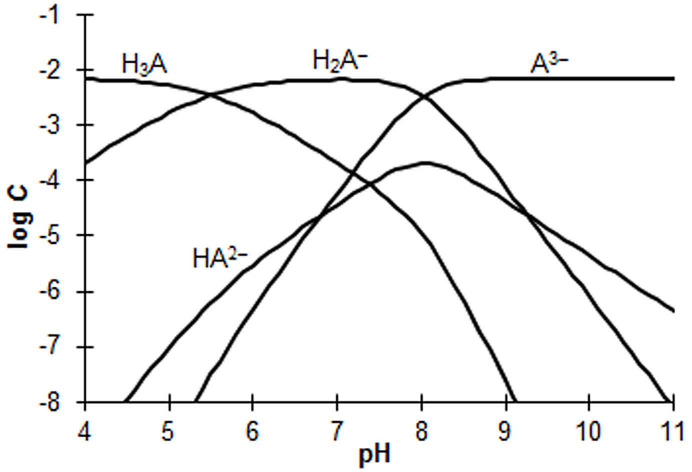
$$\mathrm{CH_3COOH + H_2O \longrightarrow CH_4 + H_2CO_3}$$

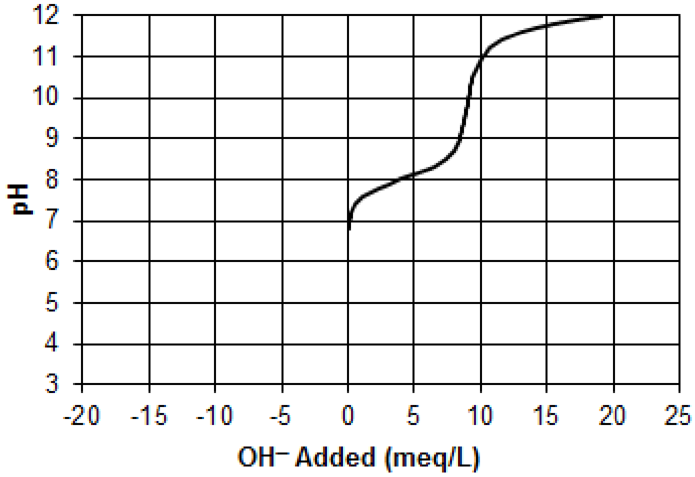
$$\mathrm{CH_3COO^- + H_2O \longrightarrow CH_4 + HCO_3^-}$$

    (a) Prepare a log C-pH diagram for the solution prior to treatment. What is the initial pH?
    (b) What concentration of NaOH must be added to adjust the solution to pH 5.2? What concentration of $\mathrm{Na_2CO_3}$ could be used as an alternative?

(c) It is proposed to add $6 \times 10^{-2}\,M$ NaOH to the original solution, after which the reaction is expected to convert 80% of the *TOT*Ac to end products. Prepare a log *C*-pH diagram for the resultant solution and find the pH before and after the biological conversion.

19. A log *C*-pH diagram for a solution containing $7 \times 10^{-3}\,M$ of a triprotic acid, H_3A, is shown below. Note that HA^{2-} is never a significant species compared to the other forms of the acid. Also shown is a base titration curve for a solution initially at pH 6.8 containing an unknown amount of *TOT*A.





(a) What is *TOT*A in the system being titrated?

(b) Hydrochloric acid (HCl) is gradually added to the pH 12.0 solution until the pH decreases to 4.5. On a copy of the preceding titration curve, sketch a plot of pH vs. HCl added, starting at the point where the previous titration ended, i.e., at (19, 12.0). The amount of acid added can be represented as negative additions of base.

20. A solution has a pH of 7.3 and an alkalinity of 25 mg/L *as CaCO₃*. Essentially all the alkalinity is contributed by the carbonate system. The water also contains $10^{-4}\,M$ Fe^{2+} (5.5 mg Fe^{2+}/L). To remove the iron, oxygen is injected into the solution, converting the Fe^{2+} to Fe^{3+}; the Fe^{3+} then precipitates as ferric hydroxide according to the following reaction:

$$\mathrm{Fe^{2+}} + \frac{1}{4}\mathrm{O_2}(aq) + 2.5\,\mathrm{H_2O} \rightleftharpoons \mathrm{Fe(OH)_3}(s) + 2\,\mathrm{H^+}$$

Calculate the pH of the water after the reactions are complete.

21. Two small streams, one of which drains an abandoned mine and is quite acidic, combine to form a larger stream. Some characteristics of the streams are provided below. Use a charge balance to estimate the DIC in Stream B, and then determine the pH, alkalinity, and DIC concentration in the combined flow.

Parameter	Stream A	Stream B
Na^+	$10^{-2.8}\,M$	$10^{-4.0}\,M$
Ca^{2+}	$10^{-4.9}\,M$	$10^{-4.1}\,M$
Cl^-	$10^{-3.0}\,M$	$10^{-4.0}\,M$
SO_4^{2-}	$10^{-3.3}\,M$	$10^{-5.1}\,M$
DIC	$10^{-5.0}\,M$	not analyzed
pH	3.4	7.7
Flowrate	50 L/min	250 L/min

22. A solution at pH 7.5 contains $2 \times 10^{-3}\,M$ *TOT*Ac, essentially all of which is consumed in a biological treatment process according to the following reactions:

$$\mathrm{C_2H_3O_2^-} + 2\,\mathrm{O_2} \longrightarrow 2\,\mathrm{HCO_3^-} + \mathrm{H^+}$$

$$\mathrm{C_2H_4O_2} + 2\,\mathrm{O_2} \longrightarrow 2\,\mathrm{HCO_3^-} + 2\,\mathrm{H^+}$$

(a) Determine the change in alkalinity, if any, that occurs if all the acetate undergoes the reaction. Express your answer in mg/L *as CaCO₃*. Assume that the solution behaves ideally.

(b) If the ionic strength of the solution in part (a) were high enough to cause the activity coefficient for species with charge of ±1 to be 0.7, how would *TOT*Ac be distributed between HAc and Ac^- in the original solution and at the endpoint of the alkalinity titration?

(c) Repeat part (a), if the reaction occurred in the solution described in part (b). Assume that $TOT\mathrm{CO_3}$ is present entirely as H_2CO_3 at the titration endpoint, regardless of the ionic strength. Keep in mind that pH is defined as $-\log a_{\mathrm{H^+}}$.

23. As noted in the chapter, many NOM molecules are acidic. As a result, water that contains NOM and low concentrations of dissolved inorganic species can be quite corrosive to both cementitious and metallic components of drinking water distribution systems. One approach for overcoming this problem is to contact the water with calcite ($CaCO_3$) to neutralize some of the acidity.

    Assume that the NOM molecules in a particular water supply can be represented as diprotic acids with $\mathrm{p}K_{a1} = 4.8$ and $\mathrm{p}K_{a2} = 7.7$, and with an average molecular weight of 250. The water, at pH 6.1, contains $5\,\mathrm{mg/L}\ \mathrm{Ca}^{2+}$ and $10^{-4}\,\mathrm{mol/L}$ $TOT\mathrm{CO}_3$ initially, and is treated in a limestone (calcite) contactor. The remaining solutes (other than the NOM) are salt ions that are neither acids nor bases. The water exiting the contactor contains $9.5\,\mathrm{mg/L}\ \mathrm{Ca}^{2+}$ and is at pH 7.9.

    (a) Using the species that are dominant in the treated water as components, write the TOTH equation for the influent solution. (Note: you will not be able to assign known values to all the terms in this expression at this point; don't let that concern you, but do fill in as many values as you can.)

    (b) Using the same conventions as in part (a), write and solve a TOTH equation for the treated water to determine the NOM concentration, in mg NOM/L.

24. A treated water supply at pH 9.54 has an alkalinity of 20 mg/L *as $CaCO_3$* and contains 8 mg/L TOTSi *as SiO_2*, present primarily as H_4SiO_4 and $H_3SiO_4^-$.

    (a) Assuming that the solution is ideal, what fraction of the alkalinity is contributed by the silica species?

    (b) Explain briefly how your answer to part (a) would change, if at all, if you discovered that the ionic strength of the solution was high enough to cause the activity coefficient of $H_3SiO_3^-$ to be 0.8. Because it is neutral, the activity coefficient of H_4SiO_4 can still be assumed to be close to 1.0.

25. A solution containing 125 mg/L butyric acid ($C_4H_8O_2$, MW 88, $\mathrm{p}K_a = 4.73$) is adjusted to pH 7.0 by addition of Na_2CO_3 and then is treated in a biological process that converts essentially all of the butyrate to carbonate species via the following reaction:

$$\mathrm{CH_3(CH_2)_2COO^- + 5\,O_2 \longrightarrow 4\,HCO_3^- + 3\,H^+}$$

    (a) Estimate the alkalinity (defined by titration to pH 4.5) after the neutralization step, but before biological treatment.

    (b) Estimate the buffer intensity of the solution in part (a) by computing the required amount of strong base to increase the pH to 7.1. Also compute the buffer intensity exactly, by using the equation given in the text.

    (c) What is the pH of the water after biological treatment?

26. A solution is made by adding $3 \times 10^{-4} M$ $Ca(OCl)_2$, $4 \times 10^{-4} M$ $CaAc_2$, $7 \times 10^{-4} M$ NH_4Ac, and $2 \times 10^{-4} M$ H_2SO_4 to water. In the pH range of 4 to 10, at what pH do you expect the buffer intensity to be largest? Explain briefly.

27. Attempt to arrange the following solutions in order of increasing buffer intensity without carrying out any calculations, and then compute the buffer intensities numerically.

    (a) $10^{-3} M$ $TOTNH_3$ at pH 7.04
    (b) $10^{-3} M$ $TOTNH_3$ at pH 9.24
    (c) $10^{-3} M$ $TOTCO_3$ at pH 8.35
    (d) $10^{-3} M$ $TOTCO_3$ at pH 6.35

28. Determine the pH and buffer intensity of aqueous solutions made by dissolving the following chemicals in pure water:

    (a) $0.1 M$ HAc plus $0.1 M$ NaAc
    (b) $0.19 M$ HAc plus $0.01 M$ NaAc
    (c) $0.02 M$ HAc plus $0.18 M$ NaAc

29. Calculate the buffer intensity of a solution prepared by adding $0.2 M$ acetic acid and $0.1 M$ sodium acetate to water, and then adjusting the pH to 5.0 by addition of NaOH.

30. Plot a curve showing the buffer intensity of a solution containing $0.1 M$ total oxalate over the range from pH 2 to 12. Under what conditions does the oxalate contribute $>90\%$ to the total buffer intensity?

31. (a) Calculate the buffer intensity at pH 6, 8, and 10 for a solution containing $10^{-2.8} M$ $TOTCO_3$.
    (b) For each of the solutions in part (a), use the calculated buffer intensity to estimate the final pH if $10^{-5} M$ NaOH is added.

32. In the metal finishing industry, "pickling" refers to the process of exposing metal parts to a strong acid solution to remove surface deposits, thereby preparing the surface for painting or other modification. An industrial wastewater from a pickling process contains $0.4 M$ $TOTSO_4$ and $0.1 M$ $TOTFe$ at pH 0.8. Iron that is incorporated into dissolved species can have a charge of either +2 or +3 (referred to as ferrous and ferric species, respectively); all the Fe in the wastewater is ferric iron. Other ions might be present in solution, but they are not acids or bases. If you use Visual Minteq in your analysis, instruct the program to ignore species that contain more than one Fe^{3+} ion, both an Fe^{3+} ion and an SO_4^{2-} ion, or both a Ca^{2+} ion and an SO_4^{2-} ion.

(a) Compute the amount of lime ($Ca(OH)_2$), in mol/L, needed to bring the solution to pH 5.5 for discharge.

(b) Develop a titration curve (pH vs. meq/L of lime added) for titration of the solution to pH 10. Report the pH after 25%, 50%, and 75% of the ultimate lime dose has been added. Ignore possible formation of $CaSO_4^o$.

(c) Compute the buffer intensity and indicate the major reactions responsible for the buffer intensity in the initial solution and at the four conditions investigated in part (b).

33. A waste solution containing $0.1\,M$ sulfuric acid is to be discharged into a body of water having a pH of 7.5 and a carbonate alkalinity of 2×10^{-3} equiv/L. To what extent must the waste be diluted (i.e., what volume of river water must be combined with a unit volume of the waste) to assure that the pH of the mixture does not drop below 6.0?

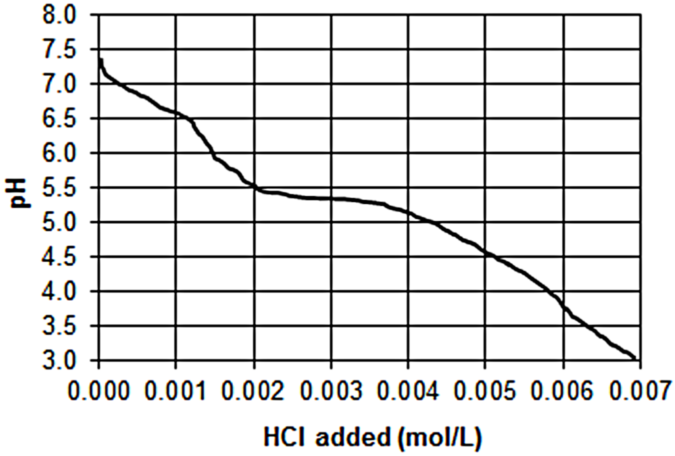
34. A titration curve is shown below for a solution with an initial pH of 7.4.

(a) What is the alkalinity of the solution, in both meq/L and mg/L *as* $CaCO_3$.

(b) For the pH range shown, at approximately what pH is the buffer intensity maximized?

(c) A species $B(aq)$ that is present in the solution is a diprotic base with $pK_{b1} = 4.0$ and $pK_{b2} = 12.0$. Write out the reactions corresponding to these pK values. Note that, for acids, the numbering of acidity constants ($K_{a1}, K_{a2}, \ldots$) starts with the most acidic species. Similarly, the numbering of basicity constants ($K_{b1}, K_{b2}, \ldots$) starts with the most basic species.

(d) When the solution equilibrates with a gas phase, $2 \times 10^{-4}\,M$ $B(aq)$ transfers out of solution and into the gas. By approximately how much does the alkalinity of the solution change, and in what direction? Explain your reasoning briefly. (Hint: It might be helpful to convert the K_b values to K_a's and determine the dominant species at different pH values.)



35. You want to prepare a solution in which the pH will remain in the range 9.8 ± 0.1 when up to $10^{-2} M$ strong acid or base is added. Noting that the target pH is close to pK_a of NH_4^+, you decide to prepare the solution by adding a mixture of NH_3 and NH_4Cl to water. What amounts of these chemicals should you add if you want to achieve the desired buffering using the minimum $TOTNH_4$?

36. An anaerobic solution in a stagnant portion of a sewer can be represented as a mixture of $5 \times 10^{-3} M$ $Na(NH_4)_2PO_4$ and $5 \times 10^{-4} M$ NaHS.

    (a) Sulfuric acid has formed on the upper surface of the pipe and is dripping into the wastewater. Prepare a plot of pH versus H_2SO_4 added for additions of 0 to $6 \times 10^{-3} M$ H_2SO_4. Ignore dilution of the wastewater by the dripping acid, and assume that, over the time frame of interest, sulfate and sulfide species are not interconvertible.

    (b) Prepare a plot of buffer intensity versus pH for the range of H_2SO_4 additions considered in part (a). For completeness, also show the data for addition of base to pH 11. At what pH in the range investigated is the solution most highly buffered?

    (c) How much acid can be added before the H_2S concentration reaches $1 \times 10^{-4} M$?

37. The acid sulfite pulping process uses sulfurous acid (H_2SO_3) to attack the lignin that holds the wood fibers together. The fibers are then released and processed into paper products, and a hot solution containing acetic acid, sulfurous acid, and some larger organic molecules is generated as a waste. This waste solution is partially evaporated and then condensed, with the smaller molecules being transferred into the evaporator condensate and the larger ones remaining behind in an organic-rich solution that can be burned to recover its energy content. The condensate can be treated in an anaerobic biological treatment process, but only if the pH is maintained near neutrality (pH 7). When the process is operating successfully, the microorganisms mediate the following reactions (CH_4 is methane):

$$CH_3COOH + H_2O \rightleftharpoons CH_4 + H_2CO_3$$

$$4\,H_2SO_3 + 3\,CH_3COOH \rightleftharpoons 4\,H_2S + 6\,H_2CO_3$$

    (Note: The Visual Minteq database includes the species $S_2O_5^{2-}$, which can form from the combination of two HSO_3^- ions and release of a water molecule. In answering the following questions, if you use Visual Minteq, exclude this species from the analysis so that your result is similar to that for a manual analysis that does not consider the species.)

    (a) Find the pH of a solution of 5000 mg/L HAc and 300 mg/L H_2SO_3-S.

(b) What would the solution pH be if all the HAc and all the H_2SO_3 were destroyed according to the above reactions, and if all the H_2CO_3 that was generated remained in solution? CH_4 undergoes no acid/base reactions. (In reality, much of the H_2CO_3 dehydrates to CO_2, which then forms bubbles along with the CH_4 and exits the solution.)

(c) How much NaOH, in mol/L, would be needed to bring the pH of the initial solution [as characterized in part (a)] to 7.0? How much Na_2CO_3 would be required to accomplish the same result? Comment on the relative requirements of these two bases, considering their relative strengths and the number of protons each can accept.

(d) If the solution pH were increased to 7.0 with Na_2CO_3 and the biological reaction then proceeded to destroy one-half of the sulfite and all the acetate according to the reactions shown, what would the final pH be?

CHAPTER 9 HOMEWORK PROBLEMS

Please re-read the note preceding the Chapter 8 Problems. The same guidelines apply to the following problems.

1. Calculate the pH of water in a cloud that has equilibrated with $SO_2(g)$ at a concentration of 1.0 ppm by volume.

2. A solution contains 2 mg/L CN^- and is at pH 8.5.
   (a) What is the concentration of $HCN(aq)$ in solution?
   (b) If the partial pressure of $HCN(g)$ above the solution is 10^{-6} atm, would HCN transfer from the gas phase into solution or from the solution into the gas, or is the system at equilibrium?

3. A solution is at pH 8.35 and has reached equilibrium with the atmosphere.
   (a) How much H_2SO_4 (mol/L) must be added to lower the pH to 6.0, if no gas/liquid exchange occurs?
   (b) Repeat part (a) if the solution remains in equilibrium with the atmosphere as the acid is added.

4. Soil water with $10^{-3}\,N$ alkalinity is in equilibrium with a soil gas in which $P_{CO_2} = 10^{-1}$ atm.
   (a) Calculate the pH and total dissolved inorganic carbon concentration (M).
   (b) If the soil water is pumped from the ground and exposed to air, what will the equilibrium pH be?

5. A soft drink has a pH around 2.7 due partially to its high H_2CO_3 content.
   (a) If all the acidity in the beverage was generated by bubbling it with pressurized CO_2, what P_{CO_2} would have been required in the bubbles?
   (b) What would the pH of the solution be if it was in equilibrium with a P_{CO_2} of 4 atm?
   (c) The pH of the solution is actually kept low by a combination of dissolved CO_2 plus phosphoric acid. Assuming P_{CO_2} is 4 atm in the bottle, what concentration of H_3PO_4 must be added to solution to reach pH 2.7?

6. Calculate the pH, alkalinity, and composition of a solution in equilibrium with a gas phase having $P_{CO_2} = 10^{-2}$ atm and $P_{H_2S} = 10^{-4}$ atm.

7. A groundwater at 25°C is initially at pH 8.0 and contains 2×10^{-3} equiv/L alkalinity.

(a) If the alkalinity is all attributable to the carbonate system, determine whether the water is undersaturated or supersaturated with respect to atmospheric CO_2.

(b) What will the pH and alkalinity of the solution be if it equilibrates with CO_2 in the atmosphere?

(c) How much CO_2 dissolves into or volatilizes out of solution as the system equilibrates with the atmosphere?

8. The surface water of a lake is at $pH = 7.9$ and contains $10^{-2.9} M$ dissolved inorganic carbon (i.e., $TOTCO_3$).

   (a) What is the alkalinity of this water?

   (b) Is the water undersaturated or oversaturated with atmospheric CO_2?

   (c) If the water equilibrates with the atmosphere, what will the final alkalinity, pH, and dissolved inorganic carbon concentration be?

9. Hydrogen sulfide gas at a partial pressure of $10^{-4.82}$ atm is in contact with a solution.

   (a) Prepare a log C-pH diagram showing the concentrations of dissolved H_2S, HS^-, and S^{2-} in equilibrium with the gas phase over the range $4 < pH < 12$.

   (b) If the solution pH is 8.5 and the S-containing species are the only contributors to alkalinity, what is the alkalinity of the solution? Assume that the solution is closed during the alkalinity titration.

   (c) Assuming that the system in part (b) remains in continuous equilibrium with the gas phase, find the pH after $5 \times 10^{-3} M$ HCl has been added to the solution. What is the change in total dissolved sulfide concentration when the HCl is added?

10. One hundred mL of air is contacted with 1 L of water at 10°C in a closed vessel. The water is initially devoid of oxygen. What are the concentration of dissolved oxygen and the partial pressure of oxygen in the air once the system comes to equilibrium?

11. What is the effect of dissolution of $10^{-4} M$ $NH_3(g)$ and $2 \times 10^{-5} M$ $H_2S(g)$ on the alkalinity of a solution that is initially at pH 8.0, if alkalinity is defined by a titration to pH 4.5?

12. The raw water supply for a community contains 18 mg/L total particulate matter and is to be treated by addition of 60 mg alum ($Al_2(SO_4)_3 \cdot 18\,H_2O$) per liter of water.

    (a) For a total flow of 8000 m^3/d, compute the daily alum requirement and the concentration of solids in the water following alum addition, assuming that all the alum precipitates as $Al(OH)_3(s)$.

(b) The water is initially at pH 7.5 and has [ALK] = 40 mg/L *as* $CaCO_3$. It is desired to maintain solution pH at 6.5 or higher. Will the pH be in the acceptable range after alum addition and $Al(OH)_3(s)$ precipitation?

(c) What will the pH be if the treated solution is bubbled with air, so that it reaches equilibrium with atmospheric $CO_2(g)$?

13. A wastewater at pH 7.5 contains 45 mg/L $SO_4{-}S$, which can be converted to sulfide species (H_2S or HS^-) under anaerobic conditions. What fraction of the sulfate can be reduced to sulfide without causing the partial pressure of H_2S in equilibrium with the solution to exceed 10^{-6} atm? Assume the solution is well-buffered at pH 7.5.

14. (a) Compare the buffer intensities of closed solutions at pH's of 3, 8, and 11, if all the solutions contain $10^{-3}\,M\ TOTCO_3$.

    (b) Repeat part (a) for open systems in equilibrium with the atmosphere (and therefore containing different concentrations of $TOTCO_3$).

15. At a Superfund site, concentrated NaOH has leaked into the groundwater, increasing the pH to 12.1 and dissolving large amounts of Si and Al from the soil (12,000 mg/L TOTSi and 1400 mg/L TOTAl). The water also contains $0.003\,M\ TOTCO_3$. One remediation strategy that is being considered is injection of CO_2 into the groundwater to lower the pH. A log C-pH diagram showing the speciation of Al and Si in the groundwater is provided below.

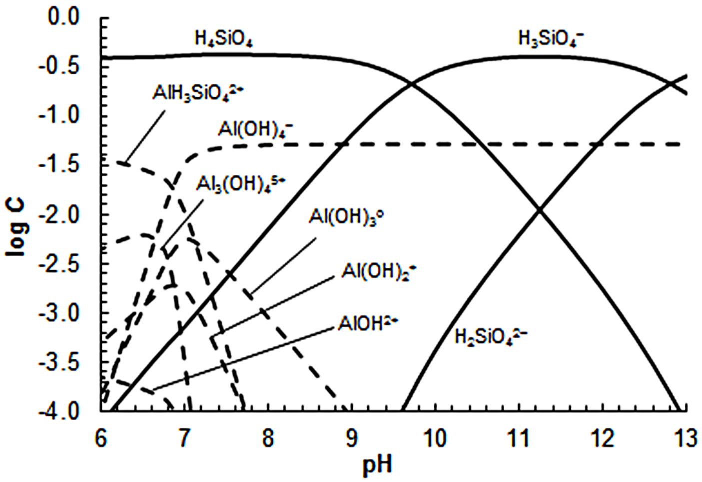
    (a) Prepare a system tableau that includes all the species that will be present in the equilibrium solution after CO_2 injection. Use the dominant Si- and Al-containing species in the original solution ($H_3SiO_3^-$ and $Al(OH)_4^-$) as components, and choose a component from the carbonate group, keeping in mind that an unknown amount of CO_2 will dissolve when $CO_2(g)$ is injected. (Hint: If you have trouble filling in any of the cells in the tableau, writing the reaction for forming the species from the components should help.)

    (b) Determine TOTH in the initial solution (before $CO_2(g)$ injection).

    (c) Write the TOTH equation for the solution after it reaches equilibrium with air, assuming that CO_2 is the only gas of interest that dissolves.

    (d) Add lines for H_2CO_3, HCO_3^-, and CO_3^{2-} to the log C-pH diagram for the solution after it has equilibrated with air.

    (e) Finally, use the log C-pH diagram in conjunction with the TOTH equation to solve for the equilibrium pH and determine how much CO_2 would dissolve into the solution (moles per liter of solution) if it reached equilibrium with air.



16. After water has been 'softened' to remove hardness ions like Ca^{2+} and Mg^{2+}, it is typically at high pH, and must be partially neutralized before being distributed. The neutralization is sometimes carried out by bubbling the solution with air.

    (a) Imagine such a water that is at pH 11.33 and contains $10^{-4}M$ each of TOTCa and TOTMg, and $2 \times 10^{-4} M$ $TOT CO_3$. Prepare a log C-pH diagram for the solution after it equilibrates with air, assuming that the solutes behave ideally. Consider Ca^{2+}, Mg^{2+}, $CaOH^+$, $MgOH^+$, and species of the carbonate group as possible solutes.

    (b) Write the TOTH equation for the solution after it equilibrates with air, and determine the equilibrium pH.

17. The water in a sewer is at pH 8.20, has an ALK of 2.50 meq/L, and contains 2.25 mmol/L $TOT CO_3$. All of the alkalinity is contributed by the carbonate and sulfide acid/base groups.

    (a) What would the partial pressures of CO_2 and H_2S be in a gas phase that has equilibrated with the solution?

    (b) What is TOTH in the solution, if H^+, HCO_3^- and HS^- are chosen as components?

    (c) As the water enters a sewage treatment plant, it is dosed with HOCl, converting all the sulfide species to sulfate. The reactions of H_2S and HS^- with HOCl are as follows:

$$H_2S + 4\,HOCl \longrightarrow SO_4^{2-} + 4\,Cl^- + 6\,H^+$$
$$HS^- + 4\,HOCl \longrightarrow SO_4^{2-} + 4\,Cl^- + 5\,H^+$$

If the HOCl dose is just enough to react with all the $TOTS(II)$, what will $TOTH$ be before any re-equilibration with the gas phase occurs. Use the same components as in part (b), along with Cl^- and SO_4^{2-}? (Hint: determine the net change in $TOTH$ that occurs for each mole of H_2S or HS^- that reacts, and then apply that information to determine the overall change in $TOTH$ when the H_2S and HS^- in the original solution undergo the reactions shown.)

18. The micro-organisms in a waste treatment pond are exposed to 35 mg/L of easily degradable organic compounds with an average composition of $C_5H_{10}O_5$. The standard molar Gibbs energy of formation of these compounds has been estimated as -2797 kJ/mol. The pond is at pH 7.3, its temperature is 25°C, and its alkalinity is 6×10^{-3} equiv/L. The overall reaction for oxidation of the organic matter is:

$$C_5H_{10}O_5 + 5\,O_2 \longrightarrow 5\,H_2CO_3$$

    (a) Due to oxygen consumption by the above reaction, the dissolved oxygen concentration in the water is only 2 mg/L. What is the maximum amount of energy that an organism could obtain by oxidizing 1 mole of the organic matter?

    (b) The operator of the treatment facility has suggested that the treatment efficiency could be improved by bubbling air through the water to encourage biological activity. Would the organisms find the environment in the untreated water more favorable, less favorable, or identical (from an energy standpoint) after bubbling with air, if the process causes the solution to equilibrate with both $O_2(g)$ and $CO_2(g)$?

    (c) Determine the pH of the system after it has been bubbled with air.

19. Two waters at 25°C are in equilibrium with air, one at pH 9.5 and one at pH 7.3. These waters are then mixed in various proportions.

    (a) Assuming that carbonate species dominate the acid/base behavior of both solutions, and that no gas transfer occurs when they are mixed, determine the alkalinity and pH of the mixture as a function of the fraction of the high-pH solution in the mixture. Consider mixing proportions such that the high-pH solution accounts for zero to 10% of the total in 0.5% increments, and then from 10% to 100% of the total in 10% increments.

    (b) For each mixture analyzed in part (a), determine whether the solution will be undersaturated, supersaturated, or in equilibrium with atmospheric

CO_2. For the 1:1 mixture, how much CO_2 will dissolve into or volatilize out of the solution as it equilibrates with the atmosphere? Express your answer in moles CO_2 transferred per liter of solution.

20. A water supply at pH 7.5 has ALK = 40 mg/L *as CaCO₃*. Essentially all the alkalinity is attributable to the carbonate acid/base system. The water is treated by addition of alum, causing $Al(OH)_3(s)$ to precipitate and aiding in the removal of colloidal matter from suspension. The precipitation of the alum generates acid by the following reaction:

$$Al_2(SO_4)_3 \cdot 14H_2O \longrightarrow 2Al(OH)_3(s) + 3SO_4^{2-} + 6H^+ + 8H_2O$$

The production of acid by this reaction lowers the solution pH. In reality, as the pH declines, the likelihood that the added Al will precipitate declines as well. Nevertheless, for this question, assume that all of the added alum undergoes the reaction shown, releasing six moles of H^+ per mole of alum added.

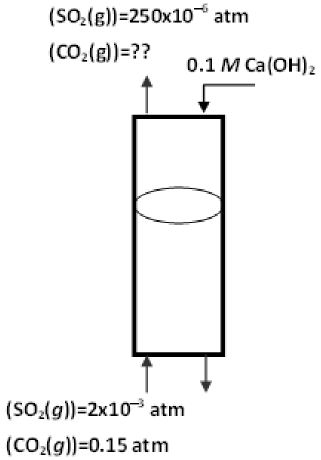
(a) Prepare a titration curve showing the pH as a function of alum added, for alum additions of 0 to 100 mg/L. (Note: you need not consider the addition of alum or the formation of $Al(OH)_3(s)$ explicitly. Rather, determine the pH as a function of H^+ added, and use the alum reaction only to convert each value of H^+ added to a corresponding alum dose.)

(b) It is determined that the optimal alum dose for coagulation is 60 mg/L. To minimize corrosion, it is desired to maintain pH $\geq$ 6.5 in the treated water. Will chemical (base) addition be necessary when the optimal alum dose is added? If so, how much? Assume that gas exchange during the various treatment steps is slow, so that the solution can be treated as a closed system.

(c) If no base is added to the solution, will it be possible to reach the target pH by bubbling the treated water with air after adding the optimum alum dose? How much CO_2 must be stripped out of solution to reach the target pH? (Hint: recall what happens to alkalinity when CO_2 is added to or removed from a solution. Also, note that the solution might reach the target pH after some CO_2 has been stripped out of the solution, but before the solution reaches equilibrium with the air.)

21. Sulfur dioxide, SO_2, is a major air pollutant emitted during the burning of sulfur-bearing fossil fuels. Consider a stack gas containing 15% CO_2 and 2000 ppm SO_2. Treatment must lower the SO_2 concentration to 40 ppm SO_2. It is proposed to absorb the SO_2 into an alkaline solution containing 0.1 mol/L $Ca(OH)_2$. The operation is counter-current, as shown in the diagram below, so the liquid effluent is in contact with the untreated influent gas. Assume the gas and liquid phases come to equilibrium rapidly, so that the water exiting the

column is in equilibrium with the gas phase that enters it. (However, the gas and liquid are not equilibrated at the top, where $Ca(OH)_2$ containing no CO_2 or SO_2 enters.) Answer the following questions to explore the feasibility and some of the potential problems associated with this process.



(a) What is the pH of the influent water? Do not consider $Ca(OH)_2$ to be a strong base for this part of the problem.

(b) What are the pH and composition of the water as it exits the reactor, i.e., in equilibrium with the influent gas? (Note that Visual Minteq accounts for the formation of $S_2O_3^{2-}$ from two H_2SO_3 molecules. If you use Visual Minteq to model the solution, instruct the program to ignore this reaction.)

(c) Do a mass balance on sulfur (flow rate in × concentration in = flow rate out × concentration out) to compute the required ratio of gas to liquid flow rates (Q_G/Q_L) in liters of gas per liter of liquid. Assume $T = 25°C$ and $P_{tot} = 1.0\,\mathrm{atm}$.

(d) Assuming $TOTCO_3$ in the influent water is negligible, do another mass balance to determine the fraction of the CO_2 that will be absorbed from the gas phase.

(e) The point of the process is to remove SO_2 from the gas. If most of the base added is used to neutralize CO_2 rather than SO_2, the process may be considered inefficient, at least in terms of reagent utilization. Of the total hydroxide consumed in the reactor, what fraction neutralizes SO_2, and what fraction neutralizes CO_2?

CHAPTER 10 HOMEWORK PROBLEMS

Please re-read the note preceding the Chapter 8 Problems. The same guidelines apply to the following problems.

1. Calculate the speciation (both concentration and activity) of zinc in seawater, based on the typical seawater composition given in Table 1.1. Assume that $TOT\text{Zn} = 5 \times 10^{-8}\,M$.

2. Prepare a log C-pH diagram for a solution containing $10^{-4}\,M\ TOT\text{Pb}$ if the only Pb complexes that form are with OH^-. Compare the diagram with the corresponding diagram for Cd in Figure 10.3 and comment on the relative acidities of Pb^{2+} and Cd^{2+}.

3. A solution at pH 7.0 contains Cu^{2+} and NH_3.

   (a) What is the ratio $(CuOH^+)/(Cu^{2+})$?

   (b) What is the ratio $(NH_4^+)/(NH_3)$?

   (c) Are there any hydroxo complexes of Cu present at concentrations greater than that of $CuOH^+$?

   (d) Use the data in the Visual Minteq database to infer values of $\log \beta_i$ for $Cu(NH_3)_i$ complexes with $1 \le i \le 4$.

   (e) Estimate the slopes of the following lines on a log C-log (NH_3) diagram for a fixed pH of 7.0, under conditions where almost all the copper is present as $Cu(NH_3)_4^{2+}$:

      (i) Cu^{2+}

      (ii) $CuOH^+$

      (iii) $Cu(NH_3)^{2+}$

      (iv) $Cu(NH_3)_3^{2+}$

4. Use the data in Tables 10.2 and 10.3 to determine equilibrium constants for the following reactions.

   (a) $Cr^{3+} + 2\,OH^- \rightleftharpoons Cr(OH)_2^+$

   (b) $Cr(OH)_2^+ + OH^- \rightleftharpoons Cr(OH)_3^\circ$

   (c) $CrOH^{2+} + H_2O \rightleftharpoons Cr(OH)_2^+ + H^+$

   (d) $Pb^{2+} + 2\,Cl^- \rightleftharpoons PbCl_2^\circ$

   (e) $PbCl_2^\circ + Cl^- \rightleftharpoons PbCl_3^-$

5. Determine the speciation of Cu, Zn, and a ligand L in a solution at pH 6.0, if the solution contains $10^{-6}\,M$ each of $TOT\text{Zn}$, $TOT\text{Cu}$, and $TOT\text{L}$, and if L participates in the following reactions:

$$Cu^{2+} + HL \rightleftharpoons CuL^{+} + H^{+} \qquad {}^{*}K_1 = 10^{6.0}$$

$$Zn^{2+} + L^{-} \rightleftharpoons ZnL^{+} \qquad K_1 = 10^{7.0}$$

$$HL \rightleftharpoons H^{+} + L^{-} \qquad K_a = 10^{-3.0}$$

6. (a) What is the speciation of mercury in an ideal solution of $10^{-4}\,M$ $HgCl_2$? What is the concentration of free Cl^- in the solution? (If you use Visual Minteq to answer the question, note that the default input component for mercuric species is $Hg(OH)_2^{o}$.)
   (b) Repeat part (a) for a solution at pH 7.0.
   (c) Repeat part (a) for a solution with a fixed Cl^- activity of 2×10^{-4}.

7. Determine the speciation of Ca, Cd, and the chelating agent EDTA in a pH 7.9 solution that contains $10^{-6}\,M$ TOTCd, $10^{-2}\,M$ TOTCa and $10^{-4}\,M$ TOTEDTA.

8. Prepare a plot of log Cd^{2+} vs P_{H_2S} for solutions at pH 8.0 and with $TOT\text{Cd} = 10^{-6}\,M$, for a range of P_{H_2S} from 10^{-6} to $10^{-3.0}$ atm.

9. Prepare a log C-pH diagram for an aqueous solution containing $10^{-6}\,M$ TOTZn and $10^{-4}\,M$ $TOT\text{NH}_3$, over the pH range from 4 to 10. What is the equilibrium partial pressure of $NH_3(g)$ in the system at pH 8.0?

10. A solution containing $0.1\,M$ each of $HgSO_4$, NaOH, and NaCl is prepared. The ionic strength of the solution is approximately $0.25\,M$.

    (a) Write mass balances for total Hg, SO_4, and Cl. Consider all the complexes that are included in the Visual Minteq database.
    (b) Determine the effective equilibrium constant, $K_{1,\text{eff}}$, for $HgSO_4$ in the solution (i.e., the equilibrium constant applicable for the given ionic strength, if the terms for the solutes are expressed as concentrations rather than activities).
    (c) Write the TOTH equation for the solution, using Visual Minteq defaults as components.
    (d) Use Visual Minteq to determine the solution pH and composition at equilibrium. What is the dominant Hg species? What fraction of TOTHg is in complexes with Cl^-? What fraction of TOTCl is complexed with Hg^{2+}?

11. In general, the fractional distribution of metal ions among their acid/base forms (i.e., Me^{n+}, $MeOH^{n-1}$, $Me(OH)_2^{n-2}$, etc.) depends only on the solution pH, and not on TOTMe. However, this generalization does not apply if polymeric species form. Explore the consequences of this fact by plotting log C-pH diagrams for solutions containing total dissolved ferric iron [TOTFe(III)] concentrations of 10^{-5}, 10^{-3}, or $10^{-1}\,M$, considering both the monomeric and

polymeric species that are included in the Visual Minteq database. At what pH does the concentrations of $Fe(OH)_3^o$ equal that of $Fe_2(OH)_2^{4+}$ in each solution?

12. (a) Use Visual Minteq to prepare a log C-pH diagram over the pH range from 3 to 12 showing Cu species in a solution of $3 \times 10^{-4} M$ $CuCl_2$, $10^{-3} M$ NH_4Cl, and $5 \times 10^{-4} M$ $Ca(OH)_2$, if the ionic strength of the solution is $0.01 M$. Show all Cu-containing species that are present at concentrations greater than $10^{-6} M$.
    (b) In the slightly alkaline pH range, the diagram indicates that the sum of the concentrations of all Cu-containing species is less than $3 \times 10^{-4} M$. Why is this the case?
    (c) What is the pH of the solution in part (a)?
    (d) What partial pressure of ammonia would be in equilibrium with the solution in part (a)?

13. Prepare a log C-pH diagram for the solution in Problem 12 if it equilibrates with a gas phase containing ammonia at a partial pressure of $10^{-6.5}$ atm. Consider pH's between 6 and 12, and continue to apply the assumption that the ionic strength is $0.01 M$. What are the two Cu species present at the highest concentrations at pH 6, 9, and 12?

14. Thiosulfate ion, $S_2O_3^{2-}$, is a complexing agent used extensively in industry. Use Visual Minteq to prepare a log C-log $(S_2O_3^{2-})$ diagram showing silver speciation in systems containing $10^{-5} M$ TOTAg at pH 9.0 and pH 13.0, over the range $-12 < \log(S_2O_3^{2-}) < -3$. In the simulation, analyze the system composition at equal increments of $\log(S_2O_3^{2-})$ (not $TOT S_2O_3$), and show all species that are present at concentrations $>10^{-12} M$.

    (a) What are the values of $(S_2O_3^{2-})$ at the points where $(Ag^+) = (AgS_2O_3^-)$ and where $(Ag^+) = Ag(S_2O_3)_2^{3-}$, for the system at pH 9? What are the corresponding values at pH 13? Explain this result.
    (b) The log C-log $(S_2O_3^{2-})$ diagram should indicate that $AgS_2O_3^-$ is dominant over a range of values of $(S_2O_3^{2-})$ at each pH. Explain briefly why $AgS_2O_3^-$ is dominant over a smaller range of log $(S_2O_3^{2-})$ at pH 13 than at pH 9.
    (c) A solution buffered at pH 9 and containing $10^{-5} M$ TOTAg is titrated with $Na_2S_2O_3$. Plot the concentration of S_2O_3-complexed Ag (i.e., the sum of the concentrations of all $Ag(S_2O_3)_x^{1-2x}$ complexes) as $TOT S_2O_3$ increases from 0 to $10^{-5} M$. What are the concentrations of all species at the end of the titration, i.e., when $TOT\text{Ag} = TOT S_2O_3 = 10^{-5} M$? Based on this result, is thiosulfate a relatively strong or weak complexing agent for silver?

15. The owner of an industry that generates wastewater containing both Ag^+ and Hg^{2+} is considering two options for discharge of the water after treatment. One option is to discharge the water through an ocean outfall, in which case the initial dilution is predicted to yield concentrations of 0.04 mg/L TOTHg and 2.5 mg/L TOTAg. The alternative is to discharge to a large river, in which the dilution would be faster and more extensive, so the total concentrations of the metals near the outfall would be lower by a factor of 10.

    Both Ag^+ and Hg^{2+} are more toxic as free ions than as complexes. The major complexing ligands in the two potential receiving waters are Cl^- (19,400 mg/L in the ocean, 35 mg/L in the river) and SO_4^{2-} (2710 mg/L in the ocean, 12 mg/L in the river). Both solutions are at pH 8.0, and the ionic strengths are 0.62 M in the ocean and 0.01 M in the river. Which disposal option would you recommend to minimize toxicity near the outfall?

16. Groundwater in a formation rich in gypsum has the following composition:

    $[Na^+] = 35$ mg/L $[Cl^-] = 48$ mg/L DIC$= 65$ mg/L
    $[SO_4^{2-}] = 110$ mg/L $[Ca^{2+}] = 116$ mg/L $TOT\mathrm{Zn} = 65\ \mu$g/L
    pH$= 7.7$

    (a) Calculate the alkalinity (meq/L) of the solution.
    (b) What are the three most abundant species of Zn and Ca in the solution, and what fraction of $TOTi$ do these species account for?
    (c) The water is pumped to the surface and placed in an an open tank, where it is dosed with $5 \times 10^{-4} M$ HCl and aerated. Determine the pH, DIC (mg/L) and ALK (meq/L) of the water after it equilibrates with air.

17. An aqueous solution at pH 7.3 contains $10^{-5} M\ TOT\mathrm{CO}_3$ and natural organic matter (NOM) at a concentration of 10 mg/L as DOC. The NOM is modeled as a mixture of two discrete ligands: L_I^-, with a charge density of 7.7 meq per gram of DOC, and L_{II}^-, with a charge density of 3.9 meq per gram of DOC. The two ligands are monoprotic acids, with pK_a's of 4.0 and 8.9, respectively.

    (a) How much alkalinity does the NOM contribute to the solution?
    (b) The solution also contains $10^{-9} M\ TOT$Pu(VI), which, in the uncomplexed form, exists as the divalent cation PuO_2^{2+}. This ion forms complexes with OH^- and CO_3^{2-}, several of which are included in the Visual Minteq database. Determine the speciation of the plutonium, ignoring the possible formation of complexes with the NOM ligands.
    (c) Now assume that PuO_2^{2+} also forms complexes with the NOM ligands, as characterized by the following reactions:

$$\mathrm{PuO_2^{2+} + L_I^- \rightleftharpoons PuO_2L_I^+} \qquad K = 10^{6.8}$$

$$\mathrm{PuO_2^{2+} + L_{II}^- \rightleftharpoons PuO_2L_{II}^+} \qquad K = 10^{7.4}$$

Determine the speciation of plutonium considering these reactions in addition to the ones considered in part (b). Note that, because the pH is known and $TOT\mathrm{CO_3}$ is much greater than $TOT\mathrm{Pu(VI)}$, the concentration ratios of inorganic Pu complexes to free $\mathrm{PuO_2^{2+}}$ remain the same as in part (b), but the absolute values of the concentrations change when complexation by the organics is taken into account. Note also that the total concentrations of the organic ligands are much larger than $TOT\mathrm{Pu(VI)}$.

18. (a) Prepare the following plots showing the speciation of mercury in solutions containing $10^{-6}\,M\ TOT\mathrm{Hg(II)}$.
    - (i) A log C-pH diagram for a solution containing $2 \times 10^{-4}\,M\ TOT\mathrm{Cl}$, a typical concentration in low-mineral fresh waters. Consider the pH range from 2 to 12.
    - (ii) Same as part (a), but for $5 \times 10^{-3}\,M\ TOT\mathrm{Cl}$, a typical concentration in brackish water.
    - (iii) Same as part (a), but for $0.5\,M\ TOT\mathrm{Cl}$, a typical seawater concentration.
    - (iv) A $\log C - \log\{\mathrm{Cl^-}\}$ diagram for a solution at pH 3.0, for $\log\{\mathrm{Cl^-}\}$ values from -5 to 0.
    - (v) Same as part (iv), but for pH 7.0.
    - (vi) Same as part (iv), but for pH 10.0.

    (b) What is the lowest pH at which a complex containing $\mathrm{OH^-}$ becomes the dominant Hg species in parts (a)(i-iii)? Why is this trend observed?

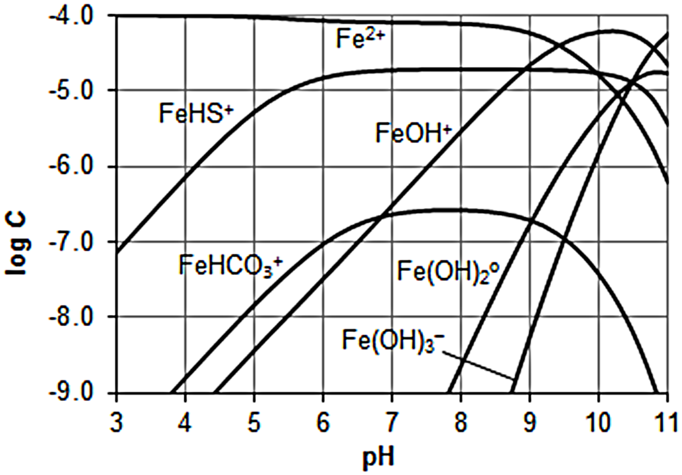
    (c) What is the lowest $\log(\mathrm{Cl^-})$ at which a complex containing $\mathrm{Cl^-}$ becomes the dominant Hg species in parts (a)(iv-vi)? Why is this trend observed?

19. A log C-pH diagram is provided below for an ideal solution containing $10^{-4}\,M$ total ferrous iron [$TOT\mathrm{Fe(II)}$], $2 \times 10^{-5}\,M$ total sulfide [$TOT\mathrm{S(II)}$], and $3 \times 10^{-4}\,M\ TOT\mathrm{CO_3}$.

    (a) If the solution is at pH 9.0, what is the total contribution (mol/L) of the six Fe-containing species to $TOT\mathrm{H}$, if $\mathrm{FeOH^+}$, $\mathrm{HS^-}$, and $\mathrm{CO_3^{2-}}$ are chosen as components?

    (b) What is the total contribution of the six Fe-containing species to the alkalinity of the solution, in equiv/L?

    (c) Using only the information provided in the plot, determine ${}^*\beta_3$ for formation of Fe−OH complexes.



20. Consider the predominance area diagram for the Fe(II)/Cl$^-$/H$_2$O system in Figure 10.19, and the equations used to develop it.

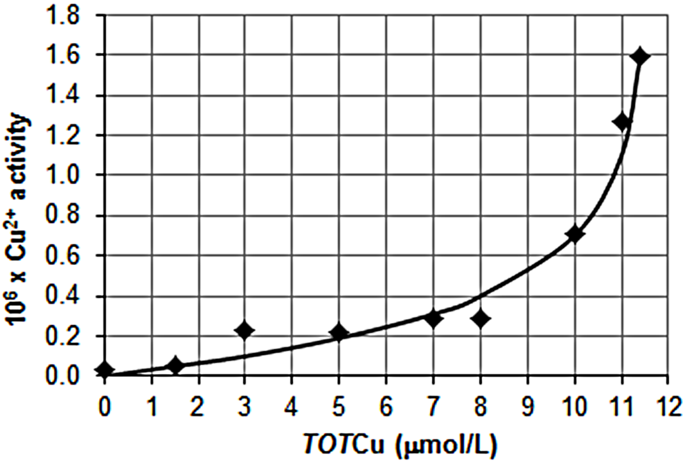
    (a) What is the predominant form of ferrous iron in a system at pH 9.2, if $\left(\mathrm{Cl}^-\right) = 0.1$?

    (b) If the chloride activity in part (a) is increased to 0.6 while the pH is held at 9.2, what will the predominant form of ferrous iron be?

    (c) If the pH of the system in part (b) is increased to 10.0, what will the predominant form of ferrous iron be?

    (d) Repeat part (c), but for a final pH of 13.

21. In a study investigating the capacity of sewage effluent to form complexes with cupric ion $\left(\mathrm{Cu}^{2+}\right)$, increasing amounts of CuSO$_4$ were added to a sample of the effluent, and the activity of Cu^{2+} was analyzed using an ion-selective electrode. The following graph shows some of the results. Assume that the ligands in the effluent can be modeled as a single species, L^{2-}, present at a concentration TOTL, and that only a single Cu$-$L complex forms. Use the results shown in the graph to estimate TOTL and the stability constant K_1 for formation of CuL(aq). The pH was low enough that Cu$-$OH complexes could be ignored.



10^6 x Cu^{2+} activity
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
1
2
3
4
5
6
7
8
9
10
11
12
*TOT*Cu (µmol/L)

CHAPTER 11 HOMEWORK PROBLEMS

Please re-read the note preceding the Chapter 8 Problems. The same guidelines apply to the following problems.

1. In some water softening operations, Mg^{2+} must be removed from solution along with Ca^{2+}. What pH is required to lower TOTMg to 10 mg/L *as CaCO₃* by precipitation of $Mg(OH)_2(s)$?

2. What is the solubility of ferrihydrite (amorphous $Fe(OH)_3(s)$) in an ideal pH 7.0 solution containing $10^{-2}\,M\ TOT\mathrm{SO}_4$? Give your answer in $\mu g/\mathrm{L}\ TOT\mathrm{Fe}$.

3. One gram of solid $Cd(OH)_2(s)$ is dispersed in a solution at pH 9.0 containing 1.0 mg/L of total dissolved Cd. The solution was prepared by adding only $Cd(NO_3)_2$ and NaOH to pure water. Do you expect some solid to dissolve, some dissolved Cd to precipitate, or no change in the solution composition?

4. A groundwater at pH 7.5 is in equilibrium with $P_{\mathrm{CO}_2} = 10^{-1.5}$ atm and with siderite ($FeCO_3(s)$). Determine the total dissolved Fe concentration.

5. A natural water sample with the following solute concentrations has been placed in a tightly sealed, headspace-free glass bottle for storage. Determine whether the solution is stable or whether calcite is expected to precipitate.

   $I = 0.012\,M$

   Alkalinity $= 1.5 \times 10^{-3}$ equiv/L

   $[\mathrm{Na}^+] = 2 \times 10^{-3}\,M$

   $[\mathrm{Ca}^{2+}] = 10^{-3}\,M$

   $[\mathrm{SO}_4^{2-}] = 10^{-3}\,M$

   $[\mathrm{Cl}^-] = 0.5 \times 10^{-3}\,M$

   pH = 8.9

6. One milligram of $NiCO_3(s)$ is added to 1.0 L of a solution containing $10^{-3}\,M$ $TOT\mathrm{CO}_3$. Over what pH range(s) will the solid completely dissolve? Assume ideal solution behavior.

7. What is the solubility of $Ca_3(PO_4)_2(s)$ in mg/L, in a solution buffered at pH 7.2 using a phosphate buffer such that $TOT\mathrm{PO}_4 = 10^{-2}\,M$?

8. An aqueous solution at pH 7.5 and containing $10^{-6}\,M\ TOT\mathrm{Cu(II)}$ is equilibrated with a gas phase having $P_{\mathrm{H_2S}} = 10^{-8}$ atm. Will covellite ($CuS(s)$) form in this system? If so, how much? If not, how much higher would $P_{\mathrm{H_2S}}$ have to be to cause the solid to precipitate?

9. Ten milligrams of gibbsite [a crystalline form of $Al(OH)_3(s)$] is added to 1.0 L of $10^{-3}\,M$ Na_2CO_3. How much aluminum will be dissolved at equilibrium, and what will the equilibrium pH be?

10. Determine the solubility of calcite, $CaCO_3(s)$, in mg/L, in pH 12 solutions of ionic strength 0.01 and $0.1\,M$. What would the solubility be in a solution with $I = 0.1\,M$ at pH 8.0? Use the Davies equation to compute activity coefficients. If you solve the problem manually, ignore the acid/base reaction of Ca^{2+}.

11. Compare the solubility of mercuric oxide [HgO(s), montroydite] in two solutions at pH 8 and with ionic strength $0.1\,M$ – one containing $10^{-3}\,M$ NaCl and the other containing $10^{-1}\,M$ NaCl. Use the Davies equation to compute activity coefficients. What is the dominant Hg species in each solution?

12. Weathering of the aluminosilicate mineral albite $\left(Na_2Al_2Si_6O_{16}(s)\right)$ can generate the clay kaolinite $\left(Al_2Si_2O_5(OH)_4(s)\right)$ via the following reaction, with $\log K = -0.68$:

$$0.5\,\mathrm{Albite} + H^+ + 4.5\,H_2O \rightleftharpoons 0.5\,\mathrm{Kaolinite} + 2\,H_4SiO_4 + Na^+$$

Determine the pH and alkalinity of groundwater with $P_{CO_2} = 10^{-1.5}$ atm that equilibrates with albite if the groundwater contains negligible amounts of solutes other than carbonate species. (Hint: Like the problems in preceding chapters, this problem requires combining known information with mass and/or charge balances and equilibrium constants. And, as usual, there are many solution approaches that can be used successfully. One approach is as follows: (1) identify all solutes expected to be present at equilibrium; (2) write the CB for the solution; (3) use the given K and reaction stoichiometry to express (Na^+) as a function of pH; (4) write other terms in the CB as a function of pH; and (5) find the pH at which the CB is satisfied.)

13. Prepare a $\log C$-pH diagram for a system in equilibrium with atmospheric $CO_2(g)$ and calcite at 15°C. Then, determine the equilibrium pH, alkalinity, and Ca^{2+} concentration for the following two solutions:

    (a) A solution for which atmospheric $CO_2(g)$ and calcite are the only inputs.
    (b) The solution in part (a) after addition of $10^{-2.7}\,M$ HCl and re-equilibration with the two nonaqueous phases.

14. "pHistory of water".

    (a) A cloud passes over a smokestack, where a raindrop absorbs $10^{-5}\,M$ H_2SO_4. Find the solution pH, assuming the droplet contains only water, the absorbed H_2SO_4, and carbonate species acquired by equilibration with the atmosphere.

(b) The droplet passes over a feedlot and comes to equilibrium with $P_{NH_3} = 10^{-10.2}$ atm while remaining in equilibrium with atmospheric CO_2. Find the new pH and the total dissolved N.

(c) Finally, the droplet falls to earth and percolates into the soil. There, it equilibrates with a rock containing amorphous silica, without any gas exchange. Prepare a $\log C$-pH diagram for the solution (droplet) at this point, covering the pH range 3 to 12 and showing all species that are present at concentrations $>10^{-12}\,M$. Find the pH and the values of $TOTCO_3$, $TOTN$, and $TOTSi$ at equilibrium.

15. The hypolimnetic (deep) water of a eutrophic lake contains $10^{-8}\,M$ total dissolved sulfide $[TOTS(II)]$. If the water is at pH 7.0 and in equilibrium with $CdS(s)$, what is the concentration of total dissolved cadmium, considering Cd complexes with HS^- and S^{2-}? (The hydrolysis of cadmium is negligible at this pH.)

16. A drinking water at pH 7.2 contains $8 \times 10^{-4}\,M$ $TOTCa$ and has an alkalinity of 80 mg/L *as $CaCO_3$*, provided entirely by species of the carbonate group. It is desired to adjust the pH of this water to cause calcite to be slightly supersaturated for purposes of corrosion control. How much lime must be added to achieve a saturation index of 0.2? What would the pH of the water be?

17. Although Mg^{2+} is soluble under most conditions encountered in natural waters and wastewaters, it can form the mineral struvite ($MgNH_4PO_4(s)$) in solutions that have relatively high concentrations of ammonia and phosphate species, such as tanks where sewage sludge is anaerobically digested.

    Consider a solution that contains $4 \times 10^{-3}\,M$ $TOTMg$, $7 \times 10^{-3}\,M$ $TOTNH_3$, and $9 \times 10^{-4}\,M$ $TOTPO_4$ and that is in contact with struvite as it exits a digester. Determine the pH values in the range 6 to 10 where additional struvite will precipitate and the values where some of the struvite on the pipe will dissolve. If you solve the problem manually, consider acid/base reactions but ignore the formation of complexes. If you use Visual Minteq, allow all complexes to be included in the calculations. The solubility constant for struvite and the corresponding reaction stoichiometry are given in Section 11.7.

18. A surface water being evaluated as a possible drinking water supply source has $pH = 7.5$ and $TOTCa = 185$ mg/L.

    (a) What is the alkalinity of the water, if it is in equilibrium with the atmosphere?

    (b) Is the water undersaturated or supersaturated with respect to calcite?

    (c) The water is to be dosed with 100 mg/L of lime, $Ca(OH)_2$. What will the new alkalinity and pH be if the lime dissolves completely, the solution re-equilibrates with the atmosphere, and no solids form? Will calcite be undersaturated or supersaturated at this point?

19. Sodium cyanide is slowly added to a solution containing a relatively small amount of mercuric ion (Hg^{2+}). Analysis of the solution composition at various points in the titration indicates that all the mercury remains in solution when small amounts of the cyanide are added, some mercury precipitates when intermediate amounts are added, and the precipitate then re-dissolves when large amounts of cyanide are added. Explain these changes.

20. An industrial wastewater at pH 6.5 contains 10 mg/L TOTCd and 100 mg/L dissolved inorganic carbon (DIC). NaOH is added to the wastewater to raise the pH to 12.

    (a) Considering $Cd(OH)_2(s)$ and $CdCO_3(s)$ as possible precipitates, will neither, one, or both of these solids begin to precipitate when the pH is first raised to 12?

    (b) Will neither, one, or both solids be present once equilibrium is attained, if the pH is maintained at 12?

    (c) What will the total dissolved concentration and the dominant dissolved species of cadmium be at equilibrium, again assuming the pH is held at 12?

21. Prepare a log C-pH diagram over the range pH 3-11 for an ideal solution in equilibrium with $Al(OH)_3(am)$. Include lines for Al^{3+} and all Al$-$OH complexes. On the same diagram, show the concentration of $Al(OH)_3(aq)$ in equilibrium with gibbsite, a crystalline aluminum hydroxide. What conclusion do you draw?

22. Zinc orthophosphate is sometimes added to water to mitigate corrosion of pipes in water distribution systems. Prepare log C-pH diagrams showing the speciation of TOTZn and $TOTPO_4$ in a system made by adding 8 mg/L $Zn_3(PO_4)_2 \cdot 4\,H_2O(s)$ to pure water. Consider both $Zn_3(PO_4)_2 \cdot 4\,H_2O(s)$ and $Zn(OH)_2(am)$ as solids that might be present at equlibrium.

23. Carbonate is sometimes added to treated drinking waters with low alkalinity to control corrosion of lead pipe and solder in the distribution system. If carbonate is added to a finished water to increase $TOTCO_3$ to $10^{-3}\,M$ and the pH to 8.0, what is the maximum concentration of dissolved lead that can be expected in the drinking water? Consider $PbCO_3(s)$, $Pb(OH)_2(s)$, and $Pb_3(CO_3)_2(OH)_2(s)$ as possible solids in the system, and also consider the formation of $PbOH^+$ and $PbCO_3(aq)$ complexes. Which solid controls Pb solubility?

24. (a) Use Visual Minteq to construct a log C-pH diagram for nickel in an industrial wastewater that contains 10 mg/L TOTNi and $10^{-4}\,M$

$TOTCO_3$. Assume the system is closed to the atmosphere, and consider the pH range 4-11. At what pH will nickel solubility be minimized, and what will the nickel concentration be in mol/L and mg/L at this pH?

(b) Repeat part (a) for an open system.

25. The owner of a limestone (calcite) quarry would like to use it to grow fish. She plans to fill the quarry with 100,000 m^3 of water that is at pH 6.9 and has equilibrated with the atmosphere. For optimal fish productivity, the pH in the quarry should be between 7.5 and 8.0.

    (a) Over time, the water is expected to equilibrate with the limestone while remaining in equilibrium with the atmosphere. How much hydrochloric acid (HCl) or caustic (NaOH) should be added to the water so that its ultimate pH is within the desired range? Give your answer in kg of chemical added.

    (b) Depending on the location in the quarry, the water might equilibrate faster with the atmosphere or the limestone. If the amount of acid or base determined in part (a) is added to the water as it is pumped into the quarry, what would the pH be at the following locations:

        i. Near the bottom of the quarry, where the solution equilibrates with $CaCO_3(s)$ but not the atmosphere;
        ii. Near the top of the quarry, where the solution equilibrates with the atmosphere but not $CaCO_3(s)$; and
        iii. At mid-depth in the middle of the quarry, where the solution does not equilibrate with either the atmosphere or the $CaCO_3(s)$.

26. A monument made of calcite has been exposed to the weathering action of atmospheric CO_2 over a period of >2500 years. Starting around 1950, the rate of weathering drastically increased, primarily as a result of the elevated SO_2 content of the atmosphere from the burning of fossil fuels.

    Assume that rainfall and P_{CO_2} have been constant over the years at 40 cm/yr and 3.8×10^{-4} atm, respectively, and that the SO_2 content of the atmosphere has been 1 ppm (by volume) since 1950. (This value of P_{CO_2} is the modern value and includes the increase since the beginning of the Industrial Age. It therefore overstates the acidity of the rain for most of the period of interest. However, the focus of this question is on the effect of the SO_2, and that effect is much greater than the effect of recent increases in the atmospheric CO_2 concentration.) Calculate the maximum possible extent of weathering (dissolution of $CaCO_3$) for the 2500 years preceding 1950 and for the period 1950 to 2010. Express the results as grams of $CaCO_3(s)$ dissolved per cm^2 cross-sectional area of the monument. Note that the actual surface area of the statue is irrelevant, because once the rain equilibrates with the solid, no more dissolution will occur, no matter how much surface area is available. However, the cross-section of the statue does matter, because that determines how much water hits it.

Carry out the calculations based on two sets of assumptions. First, assume that the rain is in equilibrium with the atmosphere before striking the monument, but that no gas exchange occurs as it drips down the monument's surface. Second, assume that the rain is in continuous equilibrium with the air as it drips. If you use Visual Minteq for these simulations, allow the program to account for nonideal solute behavior, but instruct the program to exclude consideration of $CaSO_3{}^\circ$ and $S_2O_5^{2-}$. (Note: Visual Minteq might fail to converge in some cases where calcite is input as an infinite solid. If that occurs, try inputting calcite as a finite solid with an initial concentration of 1 mol/L. If the output indicates that some calcite remains at equilibrium, then the solution will be in equilibrium with that solid and therefore will have the same composition as if it were in equilibrium with an 'infinite' amount of solid.)

27. Consider a treated domestic wastewater containing 12 mg/L $PO_4{-}P$ and with an ionic strength of $0.007\,M$. You wish to reduce the P concentration to 0.2 mg/L by precipitation of $AlPO_4(s)$.

    (a) Prepare a log C-pH diagram showing curves for the concentration of PO_4^{3-} in the untreated and treated solutions. On the same diagram, show the Al^{3+} activity that would cause the PO_4^{3-} concentration in each solution to be in equilibrium with $AlPO_4(s)$.

    (b) Alum $[Al_2(SO_4)_3 \cdot 14H_2O]$ is added to the initial solution at a dose corresponding to $10^{-3.0}\,M\ TOT\mathrm{Al}$. Add a line to the diagram representing the Al^{3+} concentration as a function of pH immediately after the alum dissolves, before any solid forms. (Hydrolysis and complexation reactions are typically faster than precipitation reactions.) At what pH values in the range $4 \leq \mathrm{pH} \leq 12$ is $AlPO_4(s)$ supersaturated?

    (c) How much alum (in mg/L) must be added to the original solution to achieve the treatment goal, if the pH is well-buffered at 7.5? Keep in mind that one Al ion precipitates for each PO_4 ion removed. For now, ignore possible precipitation of aluminum hydroxide and aluminum oxide.

    (d) Compute the Al^{3+} concentration that would be in equilibrium with gibbsite at pH 7.5 in the original solution. Discuss the consequences of this result for your answer to parts (b) and (c).

28. The solubility product for vivianite is reported as $10^{-37.76}$ in Table 11.1. What is the standard Gibbs energy of formation $(\overline{G}^\circ)$ of vivianite?

29. A drinking water source contains 170 mg/L TOTCa, has an alkalinity of 115 mg/L *as CaCO₃*, and is at pH 8.8. Answer the following questions, using Visual Minteq for the calculations.

    (a) What is Q/K for precipitation of calcite?

    (b) What would the composition of the solution be if it equilibrated with calcite? Why does the solution pH change?

    (c) To soften the water, its pH is increased to 10.8 by addition of lime. How much lime is needed, and by how much will $TOT\text{Ca}_{\text{diss}}$ be reduced, if solid/solution equilibrium is achieved? Why is the reduction in $TOT\text{Ca}_{\text{diss}}$ so limited?

    (d) What would the composition of the solution and the amount of calcite precipitated be if, instead of adding only lime, both soda ash (Na_2CO_3) and lime were added to adjust the pH to 10.8 and simultaneously achieve stoichiometric softening conditions $(TOT\text{Ca} = TOT\text{CO}_3)$?

    (e) After all the $\text{CaCO}_3(s)$ generated in part (d) is removed by settling and filtration, the softened water is recarbonated by bubbling the solution with pure $\text{CO}_2(g)$. Plot $TOT\text{Ca}_{\text{diss}}$ as a function of pH during this process, and explain why it changes in the way it does. How much CO_2 must dissolve to lower the pH to 8.5? How much CO_2 would have to dissolve to reach the same pH if the calcite removal step were not completely efficient, and 25 mg/L calcite remains in the settled water?

30. (a) Draw a log C-pH diagram showing total dissolved manganese from pH 5 to 13 in a system containing $10^{-4} M\ TOT$Mn (total in both dissolved and solid phases) and $3 \times 10^{-3} M\ TOT\text{CO}_3$. Consider the formation of all the Mn-OH and Mn-CO_3 complexes in the Visual Minteq database, and also the possible formation of pyrochroite $[\text{Mn(OH)}_2(s)]$ and $\text{MnCO}_3(am)$. On a separate graph, plot the concentrations of the two solids as a function of pH.

    (b) What P_{CO_2} would be required for both solids to be present in an equilibrium system?

31. (a) Determine the total dissolved Zn concentration in equilibrium with $\text{ZnCO}_3(s)$ in a system with $10^{-2} M\ TOT$Cl and $5 \times 10^{-3} M\ TOT\text{CO}_3$, at pH 8.0.

    (b) Draw a log C-pH diagram for a system containing $3 \times 10^{-5} M\ TOT$Zn, $10^{-2} M\ TOT$Cl, and $5 \times 10^{-3} M\ TOT\text{CO}_3$, in in which $\text{ZnCO}_3(s)$ is the only possible precipitate. Show the concentrations of the following species or groups of species in solution: Zn^{2+}, $TOT\text{Zn}_{\text{diss}}$, the sum of all Zn$-$OH complexes, the sum of all Zn$-\text{CO}_3$ complexes, and the sum of all Zn$-$Cl complexes.

(c) Repeat part (b), but this time consider possible precipitation of only $Zn(OH)_2(am)$.

(d) Re-draw the lines for (Zn^{2+}), TOTZn, and the sum of all $Zn-CO_3$ complexes from parts (b) and (c) on a separate graph. Discuss the significance of the intersection points and the implications of the graph in pH regions on the acid and base side of the intersection points. Confirm your discussion by plotting the concentrations of $ZnCO_3(s)$ and $Zn(OH)_2(am)$ in a system with the same total concentrations of Zn, CO_3, and Cl, in which both solids are considered as possible precipitates.

32. The reported composition of a groundwater is as follows.

TOTCa	467 mg/L *as $CaCO_3$*
TOTMg	257 mg/L *as $CaCO_3$*
$TOTSO_4$	470 mg/L
ALK	337 mg/L *as $CaCO_3$* (from CO_3 species)
pH	7.7

The only other ion expected to be present at a significant concentration is Na^+.

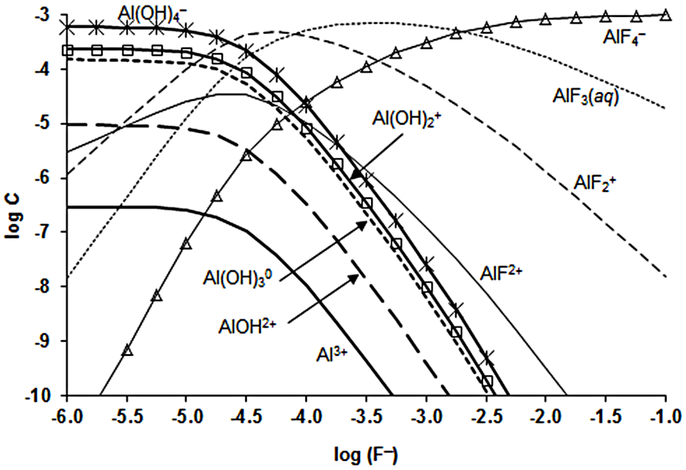
It is desired to treat the water to reduce the concentrations of all the ions listed. Consultants have recommended adding $BaCl_2$ to remove the SO_4^{2-} from solution by precipitation of $BaSO_4(s)$ ($K_{s0} = 10^{-9.98}$), and then using conventional softening to reduce the Ca^{2+} and Mg^{2+} concentrations. However, $BaCO_3(s)$ is quite insoluble ($K_{s0} = 10^{-8.57}$), so precipitation of that solid could consume much of the Ba^{2+} that is added. Determine how much, if any, $BaSO_4(s)$ can be precipitated without precipitating any $BaCO_3(s)$. Assume that the ionic strength remains the same as in the raw water. This question can be answered using either manual calculations or Visual Minteq. If you use the latter approach, you might have to add $BaCl_2$ (try $10^{-3}\,M$ or more) to the input to get the program to run successfully.

33. Both turbidity and natural organic matter can be removed from drinking water by coagulation with alum (aluminum sulfate, $[Al_2(SO_4)_3]$). When alum is added to water, Al^{3+} ions hydrolyze to form soluble monomeric $Al(OH)_y^{3-y}$ and polymeric $Al_x(OH)_y^{3x-y}$ species, and aluminum hydroxide solids $[Al(OH)_3(am)]$ can form as well.

(a) Construct a log C-pH diagram for Al(III) species in equilibrium with $Al(OH)_3(am)$. Consider the $Al-OH$ complexes in the Visual Minteq database, including the polymeric complexes $Al_x(OH)_y^{3x-y}$. Identify regions where $Al(OH)_3(am)$ precipitates in a system containing $10^{-4}\,M$ TOTAl.

(b) Use the diagram from part (a) to calculate the extent to which the solubility of Al(III) is increased if a lake water is subjected to acid precipitation and the pH decreases from 7.0 to 5.0, considering only the monomeric dissolved Al(III) species.

34. Although fluoride (F^-) forms relatively weak complexes with most metals, its complexes with Al^{3+} and Fe^{3+} are fairly strong. A log C-log(F^-) diagram for a solution at pH 6.5 that contains $10^{-3}\,M$ TOTAl is shown below, ignoring polymeric species and the possibility that a solid might precipitate.



(a) Using only the information in the graph, determine log β_3 for Al—F complexes.

(b) Is $Al(OH)_3(am)$ supersaturated at any condition(s) shown on the plot? If so, what condition(s)?

(c) A solution is well buffered at pH 6.5 and contains $10^{-3}\,M$ TOTAl. If you concluded in part (b) that $Al(OH)_3(am)$ is supersaturated under some conditions shown on the graph, determine whether precipitation could be prevented by adding fluoride, and if so, find the value of TOTF that would prevent precipitation. If you concluded that $Al(OH)_3(am)$ is not supersaturated under any conditions shown, determine what TOTAl would have to be present to cause $Al(OH)_3(am)$ to precipitate if the F^- activity were fixed at $10^{-4.5}$.

35. A wastewater at pH 7.1 containing 10 mg/L total dissolved lead and $10^{-3}\,M$ total dissolved carbonate is to be treated by raising the pH to precipitate either $Pb(OH)_2(s)$ or $PbCO_3(s)$. Although the initial solution might be supersaturated, no solids are initially present.

(a) What is the minimum lead solubility at 25°C that can be achieved?

(b) To what pH should the solution be adjusted to achieve this minimum concentration?

(c) How much caustic (NaOH) must be added to reach the pH of minimum solubility?

36. Use the Gibbs Phase Rule to determine whether it would be possible (under some theoretical, but not necessarily practical, conditions) for $AgCl(s)$, $Ag_2CO_3(s)$, and $AgOH(s)$ to all be present in an equilibrium system at standard T and P.

37. A system containing $10^{-2}M$ TOTCl and $10^{-3}M$ $TOT$$CO_3$, initially at pH 9.0, is titrated with $AgNO_3$ until $1.0M$ Ag has been added. Answer the following questions, considering the possible precipitation of three solids: $AgOH(s)$, $AgCl(s)$, and $Ag_2CO_3(s)$ ($pK_{s0} = 11.09$). Solve parts (a) and (b) using manual calculations, and part (c) using Visual Minteq.

    (Note: the questions can be answered by simulating the titration and determining the sequence of precipitation reactions, but it is also possible to reach the correct conclusion by manipulating the various solubility constants and the information about the initial solution composition without actually determining the Ag^+ concentration under the conditions of interest. If you simulate the titration using Visual Minteq, you will have to add $AgOH(s)$ to the program's database. Either approach is acceptable.)

    (a) Which solid is expected to precipitate first, and what will the activity of Ag^+ be when that occurs? How much $AgNO_3$ has been added at this point?

    (b) How high must the activity of Ag^+ be to cause a second solid to precipitate, and which solid will it be? How much $AgNO_3$ has been added when this condition is reached?

    (c) If the titration is continued, will the third solid eventually precipitate? If so, what are the conditions when this occurs? If not, explain (words or equations) why you reached that conclusion.

38. A solution that is well-buffered at pH 8.5 contains $4 \times 10^{-4}M$ total ferrous iron and $10^{-4}M$ $TOT$$CO_3$.

    (a) Do you expect either $FeCO_3(s)$ or $Fe(OH)_2(am)$, or both, to begin precipitating, based on the initial solution composition? Assume ideal solution behavior, and that Fe^{2+} and $FeOH^+$ are the only significant contributors to TOTFe in the solution.

    (b) Which solid(s) would be present if the system reached equilibrium, and what would the solution composition be?

39. Lime is sometimes added to wastewater to remove phosphorus from solution by forming a Ca$-$PO$_4$ solid. Since wastewaters typically contain $TOT\mathrm{CO}_3$ concentrations of a few millimolar, $\mathrm{CaCO_3}(s)$ might also form.

    (a) A waste contains $2\times10^{-4}\,M$ $TOT\mathrm{PO}_4$ and 2×10^{-3} equiv/L alkalinity, with the alkalinity comprised entirely of carbonate and phosphate species. Prepare a $\log C$-pH diagram showing the $\mathrm{Ca^{2+}}$ concentration that would be in equilibrium with each of two possible solid phases: calcite ($\mathrm{CaCO_3}(s)$) and hydroxyapatite ($\mathrm{Ca_5(OH)(PO_4)_3}(s)$). The reactions and corresponding equilibrium constants in the Visual Minteq database for dissolution of the two solids are:

    $$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}} \qquad K = 10^{-8.48}$$

    $$\mathrm{Ca_5(PO_4)_3OH}(s) + \mathrm{H^+} \rightleftharpoons 5\,\mathrm{Ca^{2+}} + 3\,\mathrm{PO_4^{3-}} + \mathrm{H_2O} \qquad K = 10^{-44.333}$$

    Note: Visual Minteq is not a convenient tool for addressing this question fully, but it can be used to determine the distribution of carbonate and phosphate species as a function of pH, and those results can then be used in conjunction with a spreadsheet to draw the curves for $\log(\mathrm{Ca^{2+}})$ vs. pH.

    (b) The solution in part (a) is initially at pH 8.1 and contains negligible $\mathrm{Ca^{2+}}$. Lime is added in an effort to precipitate hydroxyapatite. As the lime is added, the $\mathrm{Ca^{2+}}$ activity and the pH both increase. Which of the two solids considered in part (a) will be the first to precipitate, and at what pH does that occur?

    (c) Lime addition is continued until 95% of the initial phosphorus precipitates. How much lime has been added, and what is the solution pH, when the treatment goal is reached?

    (d) Is calcite expected to be present when the treatment goal is reached? If so, how much? If not, how much lime must be added to cause calcite to form, and what is the solution pH at that point?

40. Because cyanide is a strong complexing agent, it is used to prevent metals from precipitating in some electroplating operations. (Note: to solve this problem using Visual Minteq, you will need to add $\mathrm{HCN}(g)$ and $\mathrm{Hg(CN)_2}(s)$ to the program's database. See the appropriate sections of Chapters 9 and 11 for explanations of how to do that.)

    (a) Consider a solution at pH 10 in equilibrium with montroydite, $\mathrm{HgO}(s)$. Compute the amount of $TOT\mathrm{CN}$ that would be in solution if the overlying air had $P_{\mathrm{HCN}} = 10^{-8}$ atm. What can you conclude from the result?

(b) Consider that mercury can also form the solid $Hg(CN)_2(s)$, with $pK_{s0} = 39.28$. What concentration of *TOT*CN would be present in a pH 10 solution in equilibrium with this solid and with $P_{HCN} = 10^{-8}$ atm? Ignore the possible formation of $HgO(s)$ for this part of the problem.

(c) A solution that is well-buffered at pH 10 and that contains no Hg has equilibrated with a gas phase containing HCN at a partial pressure of 10^{-8} atm. If 0.75 *M* $Hg(CN)_2(s)$ is added to the solution, will any solid be present at equilibrium?

CHAPTER 12 HOMEWORK PROBLEMS

Please re-read the note preceding the Chapter 8 Problems. The same guidelines apply to the following problems.

1. Determine the average oxidation state of C in each of the following compounds.
   - (a) Methane (CH_4)
   - (b) Formaldehyde (CH_2O)
   - (c) Carbon monoxide (CO)
   - (d) Lactic acid ($CH_3CHOHCOOH$)
   - (e) Glutamine ($H_2NCOCH_2CH_2CHNH_2COOH$)
2. Write the oxidation and reduction half-reactions and a balanced overall reaction for each the following processes.
   - (a) Conversion of $\left(\mathrm{HOCl}+\mathrm{HS}^-\right)$ to $\left(\mathrm{Cl}^- + \mathrm{SO}_4^{2-}\right)$
   - (b) Conversion of $\left(\mathrm{CH_3OH}+\mathrm{O}_2(aq)\right)$ to $(\mathrm{CO}_2(g)+\mathrm{H_2O}(l))$
   - (c) Conversion of $\left(\mathrm{MnO}_4^- + \mathrm{Mn}^{2+}\right)$ to $\mathrm{MnO}_2(s)$
3. Determine the following values for a solution with $\mathrm{pH} = 7.0$ and $\mathrm{pe} = 8.0$.
   - (a) the $(\mathrm{Fe}^{3+})/(\mathrm{Fe}^{2+})$ ratio
   - (b) the $(\mathrm{NO}_3^-)/(\mathrm{NH}_4^+)$ ratio
   - (c) the concentration of Fe^{2+}, if the solution is in equilibrium with solid ferric hydroxide
4. What concentration of HOCl is required to oxidize 20 mg/L $\mathrm{NH_3{-}N}$ to N_2?
5. Chromium hydroxide $[\mathrm{Cr(OH)}_3(s)]$ is present in a contaminated groundwater with pH = 7.0 and pe = 4.0. Can the solution contain a significant concentration of Cr(VI) species?
6. Identify the electron donor (reductant) and the electron acceptor (oxidant), and calculate $\Delta\mathrm{pe}^\circ$, $\Delta\overline{G}_r^\circ$, and ΔE_H° for the following reactions. pe^o for conversion of $\mathrm{I}_2(aq)$ to I^- is 10.471.
   - (a) $\mathrm{Mn}^{2+} + \mathrm{H_2O} + \frac{1}{2}\mathrm{O}_2(aq) \rightleftharpoons \mathrm{MnO}_2(s) + 2\,\mathrm{H}^+$
   - (b) $\mathrm{Cl}_2(aq) + 2\,\mathrm{I}^- \rightleftharpoons 2\,\mathrm{Cl}^- + \mathrm{I}_2(aq)$
   - (c) $\mathrm{Fe}^{2+} + \frac{1}{4}\mathrm{O}_2(aq) + \mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{3+} + \frac{1}{2}\mathrm{H_2O}$

7. Determine ΔE_H for a reaction in which Ag^+ is reduced to $Ag(s)$ by oxidation of Br^- to $Br_2(aq)$ in an ideal solution at 25°C containing $10^{-4}\,M$ Ag^+, $10^{-3.7}\,M$ Br^-, and $10^{-5}\,M$ $Br_2(aq)$. Is the reaction thermodynamically favorable under these conditions?

8. In flue-gas desulfurization, $SO_2(g)$ is captured in water, where it hydrolyzes to H_2SO_3, a relatively strong acid. The sulfite ion, SO_3^{2-}, can be oxidized to sulfate by reacting with dissolved oxygen. What is the equilibrium pe in an ideal solution at pH 9.0 and with a $(SO_4^{2-})/(SO_3^{2-})$ ratio of 9? What minimum $O_2(aq)$ concentration is required to make the sulfite oxidation thermodynamically favorable under these conditions?

9. Prepare a log C-pe diagram showing the concentrations of SO_4^{2-}, SO_3^{2-}, $H_2S(aq)$, Cu^{2+}, and Cu^+, for a system at pH 8.0 that contains $10^{-4}\,M$ TOTS and $10^{-3}\,M$ TOTCu. Show data for pe values from -15 to $+15$ and log C values from -20 to -3.

10. Determine the standard potential of the following nitrification reaction. Would the standard potential change if the reaction were written with NH_4^+ as the starting material, rather than $NH_3(aq)$? If so, how much? If not, why not?

$$NH_3 + 2\,O_2(aq) \rightleftharpoons NO_3^- + H^+ + H_2O$$

11. Determine the ratio of total dissolved arsenite [As(III)] to total dissolved arsenate [As(V)] at a pH of 6.0 and a pe of 5.0, considering all the acid/base reactions that those species undergo.

12. What is the theoretical oxygen demand of cresol, C_7H_8O, in mg O_2 per mg C?

13. A water sample in which ethanol (C_2H_5OH) is thought to be the major oxidizable species is analyzed and determined to have a COD of 710 mg/L.

    (a) Write a balanced redox reaction for the oxidation of ethanol by H_2CrO_4 in the test apparatus.

    (b) What is the ethanol concentration in the original solution, in mg/L?

14. A solution at pH 7.0 contains $10^{-5}\,M$ TOTZn and $10^{-4}\,M$ TOTFe(II) and is in contact with both of the corresponding pure metals.

    (a) Determine the equilibrium constant and the value of Δpe^o for the following reaction:

$$Zn^{2+} + Fe(s) \rightleftharpoons Zn(s) + Fe^{2+}$$

    (b) Calculate the equilibrium pe in the solution.

(c) What reaction, if any, would you expect to proceed in this system?

15. Permanganate (MnO_4^-) and chlorine (Cl_2) are both strong oxidizing agents.
    (a) Write a balanced reaction for oxidation of Mn^{2+} by Cl_2, if the products are MnO_4^- and Cl^-. What is the equilibrium constant for this reaction?
    (b) Is permanganate a stronger or weaker oxidizing agent than chlorine under standard conditions?

16. (a) Which of the six species in the following redox couples is the strongest oxidant, and which is the strongest reductant: $Al^{3+}/Al(s)$, $Cu^{2+}/Cu(s)$, and Pb^{4+}/Pb^{2+}?
    (b) If an ideal solution at redox equilibrium contained $10^{-4}\,M$ each of Al^{3+}, Cu^{2+}, Pb^{4+}, and Pb^{2+}, and it also contained 1 mg/L each of $Al(s)$ and $Cu(s)$, in which direction would the following reactions proceed?

$$2\,Al^{3+} + 3\,Cu(s) \rightleftharpoons 2\,Al(s) + 3\,Cu^{2+}$$
$$2\,Al^{3+} + 3\,Pb^{2+} \rightleftharpoons 2\,Al(s) + 3\,Pb^{4+}$$
$$Pb^{4+} + Cu(s) \rightleftharpoons Pb^{2+} + Cu^{2+}$$

    (c) What would be the equilibrium composition and pe of the solution in part (b)? (Hint: try estimating the solution composition, including the pe, by imagining that the system is made by adding all the inputs in their most oxidized form, followed by the available electrons. Assume that, when the electrons are added, they bind first to the oxidized species with the greatest affinity for them, and then to other species with progressively less affinity. Finally, test whether the system speciation estimated in this way is consistent with the Nernst equation.)

17. Lead (Pb) is a powerful neurotoxin. In the past, elemental lead was used extensively in water distribution systems as the primary component of pipes, in solder, and in alloys in metal valves.
    (a) The water adjacent to some pure $Pb(s)$ in a distribution system is at pH 8.4 and contains $75\,\mu g/L$ Pb^{2+}. Estimate the pe of the solution.
    (b) How much dissolved oxygen would be present in the solution described in part (a) at equilibrium?
    (c) If the solution in part (a) contained 2 mg/L $O_2(aq)$, would oxidation of more $Pb(s)$ or reduction of Pb^{2+} be favored? What would $\Delta \overline{G}_r$ be for the reaction that is favored (written with a stoichiometric coefficient of 1 for Pb)?

18. The pore water in some lake sediments has pH$= 7.90$ and $E_H = -250\,mV$, and the $O_2(aq)/H_2O$ and S(VI)/S($-$II) redox couples have reached equilibrium in the water.

(a) If the water contains $10^{-5.10}\,M$ SO_4^{2-}, what are the concentrations of the dissolved sulfide species?

(b) What is the dissolved oxygen concentration (mol/L) in the solution?

(c) What TOTCu(II) would be present if the solution were in equilibrium with CuS(s)?

(d) What would TOTCu(I) be in the solution in part (c)?

19. Bacteria oxidize organic matter to gain energy to drive their metabolic reactions. What is the maximum amount of energy that the organisms can gain by consuming dissolved oxygen to oxidize 10^{-4} moles of TOTAc in a pH 8.0 solution containing $10^{-2}\,M$ TOTAc, if the solution is in equilibrium with atmospheric oxygen and carbon dioxide? What about at pH 6.0?

20. During turnover of a lake, reduced bottom water is mixed with oxidized surface water. Assume that bottom and surface waters with the following compositions mix in a 1:1 ratio.

$$\begin{aligned}\text{Bottom water: } & TOT\text{Fe(II)} = 1.5\times10^{-3}\,M;\ TOT\text{S}(-\text{II}) = 3\times10^{-4}\,M;\\ & (\text{SO}_4^{2-}) = 1.0\times10^{-3}\\ \text{Surface water: } & (\text{O}_2(aq)) = 3\times10^{-4}\,M;\ (\text{SO}_4^{2-}) = 1.3\times10^{-3}\,M;\\ & (\text{NO}_3^-) = 1.2\times10^{-4}\,M\end{aligned}$$

(a) Prepare a log C-pe diagram for the mixed solution. Use Visual Minteq to simulate the speciation in the solution, and assume the pH and ionic strength are fixed at 7.50 and $0.005M$, respectively. Consider the following possible oxidation states: Fe(II) and Fe(III); S($-$II) and S(VI); and N($-$III), N(0), and N(V). Also, consider Fe(II)$-$OH and Fe(III)$-$OH complexes, but ignore all other complexes and any solids that might form. Your plot should cover the ranges $-10 < \text{pe} < 15$ and $-2 > \log C > -14$. (Note: If Visual Minteq returns an error message when you scan across the whole pe range of interest, try running it twice — once from pe 0 to pe 15, and then from pe 0 to pe -10.)

(b) Add lines to the diagram for O(0) and O($-$II) species. Note that, if $O_2(aq)$ is chosen as a component, Visual Minteq automatically includes the $O_2(aq)/H_2O$ redox couple in the calculations, so you need not (and should not) specify inclusion of that couple using the “Redox” pulldown menu.

(c) Write the TOTe equation for the mixed solution, and find the solution composition at equilibrium.

21. A wastewater at pH 7.5 contains 45 mg/L $SO_4{-}S$.

    (a) What fraction of the sulfate can be reduced to sulfide without causing the partial pressure of H_2S in equilibrium with the solution to exceed 10^{-6} atm? Assume the solution is well-buffered at pH 7.5.

    (b) If the H_2S partial pressure reached 10^{-6} atm and the solution contained 0.1 mg/L *TOT*Zn, would you expect wurtzite [$ZnS(s)$] to precipitate?

22. A lake water at pH 6.5 contains $1 \times 10^{-3}\,M$ SO_4^{2-} and $10^{-5}\,M$ *TOT*[S(−II)]. Assuming the solution is at equilibrium with respect to redox reactions, determine the pe of the water. What is the equilibrium value of P_{O_2}?

23. Re-run the simulation in Example 12.12, but without the assumption that the pH remains constant. What are the equilibrium pe and pH of the water in this case? Are any solids supersaturated in the solution?

24. A well water at 25°C and pH 8.40 contains 4 mg/L *TOT*Fe(II) and is in equilibrium with siderite [$FeCO_3(s)$], with which it was in contact underground (no solids are in the water collected in the well). When the water is brought to the surface, it is aerated, thereby oxidizing essentially all of the Fe(II) to Fe(III) and causing precipitation of ferrihydrite [$Fe(OH)_3(s)$]. The aeration also equilibrates the solution with atmospheric CO_2. Assume that the solution behaves ideally.

    (a) What is the alkalinity of the untreated water? If you solve the problem manually, assume that the only significant dissolved Fe(II) species at pH 8.40 are Fe^{2+} and $FeOH^+$, and that the concentrations of HCO_3^- and CO_3^{2-} are negligible at the alkalinity endpoint.

    (b) Write a balanced reaction for oxidation of Fe^{2+} by dissolved oxygen to form ferrihydrite, and determine the alkalinity of the treated water (i.e., after oxidation of the Fe(II) and equilibration of the solution with atmospheric CO_2). Consider only the dissolved species, not the solids, as possible contributors to the alkalinity. Keep in mind that both the Fe^{2+} and the $FeOH^+$ in the original solution are oxidized to $Fe(OH)_3(s)$.

    (c) Assuming that the pH after the oxidation step is <5.0, approximately how much CO_2 is exchanged between the solution and the gas bubbles during the aeration step, and in what direction is the exchange? Express your answer in moles of CO_2 exchanged per liter of water.

25. A groundwater that is well buffered at pH 7.7 contains $5 \times 10^{-3}\,M$ *TOT*CO_3, $3 \times 10^{-6}\,M$ *TOT*As(III), $3 \times 10^{-7}\,M$ *TOT*As(V), and no dissolved oxygen. In general, it is much easier to remove As(V) than As(III) from solution, so you wish to oxidize the As(III) in preparation for a subsequent treatment step to remove the arsenic from the water. You have chosen to explore whether that

oxidation might be accomplished by addition of $1.6 \times 10^{-6}\,M$ potassium permanganate ($KMnO_4$), which you hope will undergo reactions like the following:

$$5\,H_3AsO_3 + 2\,KMnO_4 \longrightarrow 5\,HAsO_4^{2-} + 2\,K^+ + 2\,Mn^{2+} + 3\,H_2O + 4\,H^+$$

(a) Develop a $\log C$-pe diagram showing the major species of all the redox-active groups in the system at pH 7.7. Consider pe values from -10 to 15 and $\log C$ values from -10 to -4. (Note: To answer the subsequent parts of the question, it will be useful to re-draw the $\log C$-pe diagram for smaller pe ranges, as needed.)

(b) What is the equilibrium pe of the system after the $KMnO_4$ has been added? Assume that the $O_2(aq)$/H_2O redox couple is not active. If the system reaches equilibrium, will the treatment objective be achieved?

(c) Repeat part (b) assuming that the $O_2(aq)/H_2O$ couple participates in the redox reactions. Will the treatment objective be achieved in this case? How will the composition of the equilibrium solution differ from that in part (b)?

26. Mercuric salts were a common waste product from the manufacture of plutonium in nuclear weapons production facilities, with concentrations approaching $10^{-2}\,M$ in some solutions. Wastewater containing these mercuric salts was disposed of in unlined lagoons, and the water from these lagoons sometimes leaked into the local aquifer. Under reducing conditions in the aquifer, the pe of the water could decline, resulting in the reduction of the Hg(II) to dissolved or liquid elemental mercury [$Hg(aq)$ or $Hg(l)$, respectively].

    Determine the equilibrium speciation of Hg in an aquifer at a pe of 8.0 and a pH of 7.0, if $TOTHg_{\text{diss}}$ is $10^{-4}\,M$. Consider Hg(0) and Hg(II) species. Would precipitation of $Hg(l)$ be thermodynamically favorable in this solution? $\overline{G}^{\circ}_{Hg(aq)} = 37.3$ kJ/mol.

27. Reference electrodes are sometimes constructed based on the $Cu(s)$/$CuSO_4$ redox couple by immersing a copper wire in a solution that contains crystals of $CuSO_4 \cdot 5\,H_2O$ (chalcanthite, with $\log K_{s0} = -2.64$). A porous frit or membrane allows dissolved species to exchange between the solutions inside and outside the electrode. As long as chalcanthite is present inside the electrode, the activities of the redox species (and therefore the redox potential) in the reference solution remain constant, which is a key requirement for an effective reference electrode. In the following calculations, assume $T = 25°C$ and that the solutions are ideal.

    (a) What are the pH and the composition of a solution made by equilibrating chalcanthite with pure water, ignoring redox reactions? Use Visual Minteq, and allow the program to determine the ionic strength and activity coefficients. (You might need to indicate that the initial solution contains small, equal concentrations of TOTCu(II) and $TOT\mathrm{SO_4}$.)

(b) What is the redox potential of the electrode solution, assuming that the Cu(s) equilibrates with Cu(II) species in solution, but that the redox reactions do not significantly change the total dissolved Cu(II) concentration?

(c) Test the assumption in part (b) by computing the equilibrium concentration of TOTCu(I) at the computed pe. Similarly, determine if a significant fraction of the $TOT\mathrm{SO_4}$ would be converted to sulfite (i.e., S(IV)) species.

28. You wish to explore whether iron filings could be used to remove dissolved mercury from a pH 1.5 solution that contains $180\,\mu\mathrm{g/L}$ TOTHg(II), $10\,\mathrm{mg/L}$ TOTFe(II), and $10^{-3}\,M$ TOTCl(−I). In theory, the added iron could react with either the Hg(II), reducing it to Hg(l), or with $\mathrm{H^+}$, reducing it to $\mathrm{H_2}(aq)$, which could then migrate out of solution.

    (a) What are the dominant Fe(II) and Hg(II) species in the initial solution?

    (b) Compare the Gibbs energies of reaction for reactions of the filings (i.e., metallic iron) with each of the possible oxidants ($\mathrm{H^+}$ and $\mathrm{Hg^{2+}}$) at 25°C, assuming that $\mathrm{H_2}(aq)$ is in equilibrium with the atmosphere. Repeat the calculation for reaction of the filings with the form of Hg(II) that you determined to be dominant in part (a). Give all answers in kJ per mole of Fe. Which reaction is most favorable from a thermodynamic perspective?

29. A soil solution contains $10^{-5}\,M$ TOTMn(II), $10^{-2}\,M$ $TOT\mathrm{CO_3}$, and $4\,\mathrm{mg/L}$ dissolved $\mathrm{O_2}$, and is at pH 7.5. The dissolved manganese is present primarily as either free $\mathrm{Mn^{2+}}$ ions or as $\mathrm{MnCO_3}(aq)$ complexes ($K_1 = 10^{4.70}$).

    (a) Determine whether the solid rhodocrocite [$\mathrm{MnCO_3}(s)$] is undersaturated, saturated, or supersaturated in the solution.

    (b) The Visual Minteq database includes the reaction shown below for formation of the mineral manganite. What are the chemical formula for manganite and the oxidation state of Mn in that solid?

    $$\mathrm{Mn^{2+}} + 2\,\mathrm{H_2O} \rightleftharpoons \text{Manganite} + 3\,\mathrm{H^+} + \mathrm{e^-}$$

    (c) Will either manganite or rhodocrocite be present if the soil solution reaches redox equilibrium? If so, how much and which solid(s) will be present? If not, how much $\mathrm{Mn^{2+}}$ would have to be present to induce precipitation of one of the solids? In either case, assume that the pH is well buffered.

30. A metal undergoes the following two redox half-reactions:

$$\mathrm{Me^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Me^{2+}} \qquad E_H^{\mathrm{o}} = 0.53\,\mathrm{V}$$

$$\mathrm{Me^{3+}} + 3\,\mathrm{e^-} \rightleftharpoons \mathrm{Me}(s) \qquad E_H^{\mathrm{o}} = 0.87\,\mathrm{V}$$

What potential would be measured if a cell with an SHE were connected to a cell containing an electrode made of Me(s) in a solution of $0.1\,M$ Me^{2+} at 25°C? Assume ideal solution behavior and that the ions can migrate between the cells through an ion-permeable membrane. Which electrode is the cathode and which is the anode?

31. Arsenic(V) can be removed from drinking water readily by adsorption to hydrous ferric oxide [FeOOH(s)], but As(III) is much more difficult to remove. One treatment approach that has been explored is to pass the water through a bed containing pyrolusite [$MnO_2(s)$] pellets prior to contacting the water with FeOOH(s), in the hope that the $MnO_2(s)$ will oxidize the As(III) to As(V). The following reaction is included in the Visual Minteq database for formation of pyrolusite:

$$Mn^{2+} + 2\,H_2O \rightleftharpoons \text{Pyrolusite} + 4\,H^+ + 2\,e^- \qquad \log K = -41.38$$

(Remember that Visual Minteq shows the stoichiometry for formation of solids, but the $\log K$ for their dissolution. The sign of $\log K$ given here has been reversed from that in the database, so that it applies to the reaction as shown.) Consider a solution that is well buffered at pH 8 and that initially contains $10\,\mu g/L$ TOTMn(II), $25\,\mu g/L$ TOTAs(III) and $10\,\mu g/L$ TOTAs(V). The solution is then dosed with 0.1 mg/L pyrolusite. Assume that all the dissolved Mn(II) is present as Mn^{2+}.

   (a) Write a balanced reaction for oxidation of As(III) to As(V) by reduction of pyrolusite to Mn(II). Use pyrolusite as one reactant, and the dominant dissolved species in each oxidation state for the other reactants and products. What pe would be required for each half-reaction to be at equilibrium? Do you expect the desired reaction to proceed?

   (b) Compute the composition of the system once it reaches equilibrium, assuming that water is not redox-active.

32. Prove using the Gibbs phase rule that a solution cannot be in redox equilibrium and also be in gas/liquid equilibrium with the atmospheric partial pressures of O_2 and H_2. Consider a system in which the total pressure and temperature are fixed at 1 atm and 25°C, respectively.

33. In systems where methane is being generated by fermentation of organic matter, the overall process is typically modeled as a two-stage sequence that generates acetate and molecular hydrogen in the first stage and then consumes them in the second (via two separate reactions). $CO_2(g)$ is also generated as part of the process, and the various gases bubble out of the solution.

    For example, the reaction sequence for fermentation of butyrate ($C_3H_7COO^-$, $pK_a = 4.82$) is shown below.

$$\text{1st stage:}\quad C_3H_7COO^- + 2\,H_2O \rightleftharpoons 2\,CH_3COO^- + 2\,H_2(g) + H^+$$

$$\text{2nd stage:}\quad CH_3COO^- + H^+ \rightleftharpoons CH_4(g) + CO_2(g)$$
$$CO_2(g) + 4\,H_2(g) \rightleftharpoons CH_4(g) + 2\,H_2O$$

(a) If the hydrogen partial pressure in the system becomes too large, the first reaction is impeded, and the process can fail. For a system at pH 6.8 that contains $2.0 \times 10^{-3}\,M$ *TOT*But and $1.0 \times 10^{-2}\,M$ *TOT*Ac, what is the maximum partial pressure of $H_2(g)$ that will allow the first reaction to proceed? The standard molar Gibbs energy of formation of butyrate is 350.4 kJ/mol; all other values needed to solve the problem can be obtained from the text.

(b) If the process generates gas bubbles that contain 45% $CO_2(g)$ and 55% $CH_4(g)$, what is the minimum partial pressure of $H_2(g)$ that is needed for the second reaction in the second stage to proceed?

(c) What is the alkalinity of the untreated solution in mg/L *as $CaCO_3$*? How does the overall reaction affect the alkalinity of the solution (increase, decrease, or no change), assuming that the process is working properly so that virtually all of the acetate and $H_2(g)$ being generated by the first reaction are consumed at the same rate by the latter reactions?

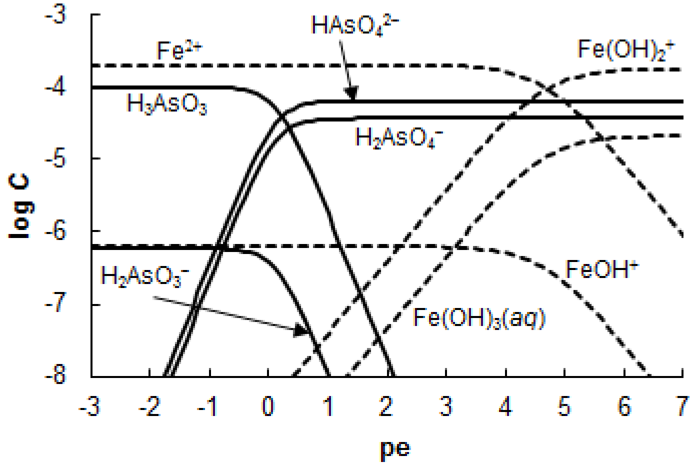
34. Plot a log *C*-pe diagram for bromine species in a solution containing 0.25 mg/L *TOT*Br at pH 7.5. Consider Br^-, HOBr, OBr^-, and BrO_3^-. What would the equilibrium speciation of Br be in a solution initially containing 0.25 mg/L Br^- and 25 mg/L Cl^-, if HOCl were added at a dose of 2 mg/L *as Cl_2*.

35. The following graph indicates the speciation of the As(V)/As(III) and the Fe(III)/Fe(II) redox couples at pH 7, for a system containing $2 \times 10^{-4}\,M$ *TOT*Fe and $1 \times 10^{-4}\,M$ *TOT*As, and in which no solids precipitate. To minimize clutter, only the two most dominant species of each element in each oxidation state are shown. All the lines continue without changing slope as they extend beyond the pe region shown.

(a) Identify the strongest oxidizing agent and strongest reducing agent among the species shown.

(b) A solution containing $2 \times 10^{-4}\,M$ $FeCl_2$, $5 \times 10^{-5}\,M$ Na_3AsO_3, and $5 \times 10^{-5}\,M$ Na_3AsO_4 is well-buffered at pH 7. What will the equilibrium pe and solution composition be? Assume that redox reactions of water are kinetically inhibited.

36. An aluminum pot is filled with tap water at pH 7.0 that contains 25 mg/L Cl^- and 1 mg/L *TOT*OCl *as Cl_2*. What is $TOT\text{Al}_{\text{diss}}$ in the solution after it equilibrates?



37. A solution that is buffered at pH 7.0 contains 10 mg/L *TOT*Cr(VI). Ferrous sulfate ($FeSO_4$) is added to the solution to provide 10 mg/L of *TOT*Fe(II). Write a redox reaction between Fe^{2+} and $HCrO_4^-$ that generates $Fe(OH)_3(s)$ and $Cr(OH)_3(s)$ as products.

    (a) After 1 mg/L of Fe(II) has reacted, both solids are present in the solution. What is the molar Gibbs energy of reaction for the redox reaction under these conditions?

    (b) Compute E_H of each half-cell reaction, and ΔE_H of the overall redox reaction under the conditions specified in part (a).

    (c) What is the concentration of *TOT*Fe(II) at equilibrium?

    (d) Repeat part (b) for the equilibrated solution.

38. Use Visual Minteq to find the equilibrium composition of a solution made by adding 1.0 g nantokite [$CuCl(s)$] to 1.0 L of pure water. Consider the possibility that the nantokite might partially or completely dissolve, and also that it might disproportionate to form Cu(II) and Cu(0). Allow the program to determine the equilibrium pe, pH, and ionic strength. (Hint: if the program returns an error message, try including a very small, but nonzero, input concentration of Cu^{2+} [e.g., $10^{-12}\,M$].)

39. Hexavalent chromium (Cr(VI)) can exist as either a monomer ($H_xCrO_4^{x-2}$) or a dimer ($Cr_2O_7^{2-}$). H_2CrO_4 is chromic acid, and $Cr_2O_7^{2-}$ is dichromate ion. Cr(VI) is used extensively in several industries, including metal processing and leather tanning; it also used to be used as an oxidant to destroy organic matter in a number of applications (e.g., COD tests, cleaning laboratory glassware), although those uses are diminishing.

Because Cr(VI) is a carcinogen, its discharge into receiving waters and sewage systems is tightly regulated, and efforts are being made to reduce or eliminate its use in many of these applications. In situations where Cr(VI) is still used, the most common approach for removing it from wastewater is to reduce it to Cr(III), a much less toxic and less soluble form of Cr. The reduction is sometimes accomplished by addition of Fe(II) to the water.

(a) Prepare a $\log C$-pe diagram for a pH 5 system containing $1.1 \times 10^{-3}\,M$ TOTCr and $3 \times 10^{-3}\,M$ TOTFe.

(b) Write the TOTe equation for a system made by adding $3 \times 10^{-3}\,M$ $FeCl_2$ to a pH 5.0 solution that contains $1.1 \times 10^{-3}\,M$ Cr(VI) and no Cr(III). Assuming the system is well-buffered at this pH, what are the approximate values of pe and TOTCr(VI) at equilibrium?

40. Recall from Chapter 11 that chelating agents are sometimes added to solutions to prevent the precipitation of metals. Although such chelating agents might be advantageous in a production process, their presence in the waste stream produced by such processes is often problematic. You have been asked to recommend a treatment process to remove copper from a solution at pH 1.0 that contains $5 \times 10^{-3}\,M$ each of Cu^{2+} and TOTEDTA. Determine the minimum concentration of $TOT\mathrm{Cu}_{\mathrm{diss}}$ that could be attained by increasing the solution pH to any desired value between 1 and 13 by precipitation of $Cu(OH)_2(s)$. Compare that concentration with the concentration that could be achieved by adding metallic aluminum to the solution to reduce the Cu^{2+} and precipitate it as $Cu(s)$, if the solution remains at pH 1.0. Consider the acid/base chemistry of Cu^{2+}, Al^{3+}, and EDTA in the first part of the problem, and the Cu(II)/Cu(0) and Al(III)/Al(0) redox couples in the second part. (Note: this question is based on a waste treatment process developed and used in the 1990s by the Boeing Co., in which scrap aluminum was added to a waste solution to precipitate strongly chelated Cu(II). The process worked well, but had to be abandoned when it was determined that, under some circumstances, HNO_3 in the waste was being reduced to the potentially toxic gases $NO(g)$ and $NO_2(g)$.)

CHAPTER 13 HOMEWORK PROBLEMS

Please re-read the note preceding the Chapter 8 Problems. The same guidelines apply to the following problems.

1. Stillings et al. (1998)[5] report the following data for adsorption of oxalate species onto a natural aluminosilicate mineral. The data were collected in solutions at pH 3 to 5, but the authors found that the total adsorption of oxalate was independent of pH in this range.

   (a) Estimate best-fit parameters to model the data according to the Langmuir and Freundlich isotherms.

   (b) Use the isotherms derived in part (a) to estimate the adsorption density at an equilibrium dissolved oxalate concentration of 10 mmol/L. Which estimate would you use if you needed to predict q_{Ox} for those conditions?

$\{\mathrm{Ox}\}_{\text{diss, eq}}$, mmol/L	q_{Ox}, μmol/m^2	$\{\mathrm{Ox}\}_{\text{diss, eq}}$, mmol/L	q_{Ox}, μmol/m^2
0.00	0.00	3.45	16.84
0.65	8.03	3.49	18.17
0.94	6.50	3.54	18.07
1.00	2.60	6.50	23.69
1.54	16.74	6.53	23.38
1.65	11.52	6.81	18.20
1.93	10.93		

2. In many water treatment plants, contaminants are removed from the feed solution as it flows through a column packed with adsorbent particles; a similar process can occur as groundwater flows through soil particles. Such systems are sometimes modeled as a series of batch reactors containing adsorbent, with flow of water represented by movement from one batch reactor to the next.

   The compound methyl-isoborneol (MIB) can give water an earthy-musty odor, even at concentrations of just a few ng/L. Gillogly et al.[6] reported that MIB sorption from a pure water (no competing adsorbates) onto activated carbon (AC) can be characterized by $q = 9.6c^{0.5}$, where q is in ng MIB/mg AC and c is in ng/L. Compare the equilibrium dissolved MIB concentration in a system in which 5 mg AC/L is added to a single batch reactor with that in a system in which the water flows through four batch reactors in series, each containing 1.25 mg AC/L, if the initial MIB concentration in the water is 100 μg/L.

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[5] Stillings, L.L., Drever, J.I., and Poulson, S.R. (1998) "Oxalate adsorption at a Plagioclase (An_{47}) surface and models for ligand-promoted dissolution." *Environ. Sci. Technol. 32*, 2856-2864.

[6] Gillogly, T.E.T., Snoeyink, V.L., Elarde, J.R., Wilson, C.M., and Royal, E.P. (1998). "^{14}C-MIB adsorption on PAC in natural water." *Journal AWWA 90*(1), 98-108.

3. In a study of sorption of arsenate and sulfate onto an ion exchange resin, both adsorbates obey Langmuir isotherms. When the resin is initially loaded with Cl^- and only one of the adsorbates is present, K_{ads} is $0.12\ L/\mu mol$ for $TOT\,AsO_4$ and $1.20\ L/\mu mol$ for $TOT\,SO_4$, and q_{max} is $150\,\mu mol/g$ for both adsorbates. Compare the dose of resin required to reduce the arsenate concentration from 1.0 to $0.07\,\mu mol/L$ in solutions initially containing negligible and $150\,mg/L$ $TOT\,SO_4$.

4. Equation (13.23) suggests that if multiple adsorbents are present in a system, each one behaves independently, and they are linked only through the fact that they must all equilibrate with the same solution. However, there are cases where the assumption of independence among adsorbents fails. For instance, Figure 13.31 shows a case where adsorption decreased when a second adsorbent was added. Suggest some possible explanations for this observation.

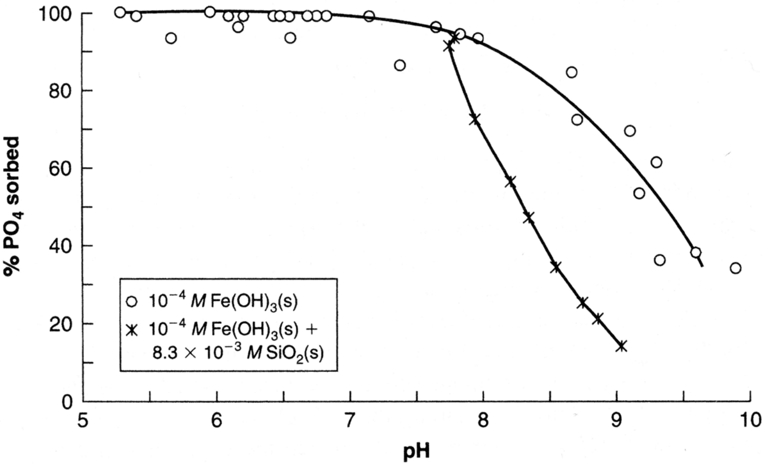

Figure 13.31. Fractional removal of $10^{-6}\,M$ phosphate from two solutions containing $10^{-4}\,M$ $Fe(OH)_3(s)$. Phosphate does not sorb onto $SiO_2(s)$ under these conditions, and the addition of $SiO_2(s)$ to the system containing $Fe(OH)_3(s)$ causes sorption of phosphate to decrease [from Anderson and Benjamin[7]].

5. Data for sorption of Cd onto ferrihydrite ($Fe(OH)_3(s)$) are shown in Figure 10.5 for solutions with ionic strength $0.7\,M$ and containing substantial concentrations of NO_3^-, Cl^-, and/or SO_4^{2-}. Cd^{2+} forms complexes with Cl^- and SO_4^{2-}, but not with NO_3^-. One hypothesis to explain the data is that free Cd^{2+} can adsorb to the solid, but complexed Cd species cannot. In carrying out the following calculations, assume that the ionic strength affects the activity of solutes, but not that of adsorbed species.

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[7] Anderson, P.R., and Benjamin, M. (1990) "Surface and bulk characteristics of binary oxide suspensions." *Environ. Sci. Technol. 24*(5), 692-698.

Based on the data point where 50% of TOTCd is adsorbed in the absence of the ligands, estimate the apparent equilibrium constant for the following reaction: $\equiv\text{FeOH} + \text{Cd}^{2+} \rightleftharpoons \equiv\text{FeOCd}^{+} + \text{H}^{+}$. Then, use this value of K_{ads} to model the pH-sorption edge for the solution containing 0.5 M Cl^-, assuming that Cd$-$Cl complexes cannot adsorb and that, in the pH range of interest, essentially all the surface sites are singly protonated (i.e., ignore the species $\equiv\text{FeO}^-$ and $\equiv\text{FeOH}_2^+$). Compare the predictions with the experimental results.

6. In 'ligand-promoted dissolution' processes, dissolution of a solid is thought to proceed via adsorption of the ligand, complexation of a metal ion in the solid's surface layer, and release of the complex into solution. Often, the rate of dissolution is proportional to the adsorption density of the ligand, as shown in Figure 13.32a. However, in other cases, almost no dissolution occurs until enough complexing agent has been added to saturate the available surface sites, as shown in Figure 13.32b.

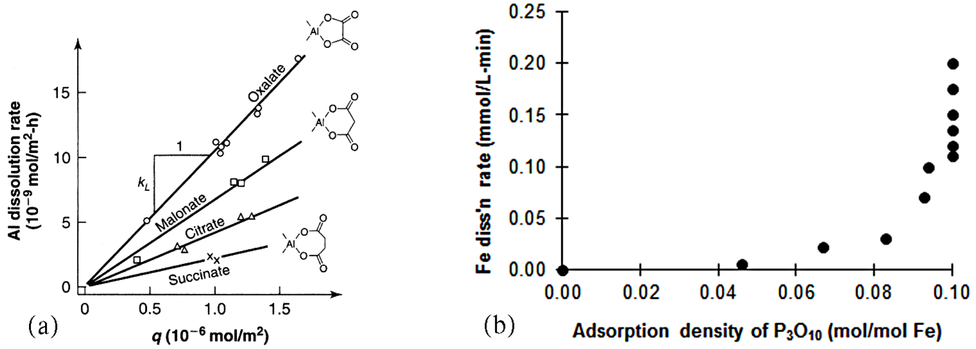

Figure 13.32. (a) Enhancement in the rate of dissolution of $\text{Al}_2\text{O}_2(s)$ attributable to the presence of four carboxylic acids [from Furrer and Stumm[8]]. (b) Increase in the dissolution rate of ferrihydrite by addition of P_3O_{10}. q_{max} is 0.10 mol P_3O_{10}/mol Fe. The data points at the far right progress upward as more P_3O_{10} is added to the system, all of which remains in solution because $q = q_{\text{max}}$ [from Lin and Benjamin[9]].

By writing out all the reactions that you expect to take place in such systems and considering the different ways that these reactions might compete with one another, suggest an explanation for the different types of behavior. (Hint: tripolyphosphate species ($\text{H}_x\text{P}_3\text{O}_{10}^{5-x}$) are much stronger complexing agents and also much stronger adsorbates that the other ligands shown.)

7. Ferrihydrite is to be used to treat a photo processing waste solution that contains

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[8] Furrer, G., and Stumm, W. (1986) "The coordination chemistry of weathering: I. Dissolution kinetics of δ-Al_2O_3 and BeO." *Geochimica Cosmochimica Acta 50*(9), 1847-1860.

[9] Lin, C.F., and Benjamin, M.M. (1990) "Dissolution kinetics of minerals in the presence of sorbing and complexing ligands." *Environ. Sci. Technol. 24*(1), 126-134.

Ag^+, $S_2O_3^{2-}$, Na^+, and NO_3^-. Any of these ions can adsorb to the ferrihydrite surface, with the former two binding much more strongly than the latter two. Write the reactions that would have to be considered to compute the equilibrium composition of the solution, and prepare the input table to model the system using the Triple Layer Model within Visual Minteq. Consider acid/ base reactions of the surface, sorption of the four free ions, complexation of Ag^+ with $S_2O_3^{2-}$, and sorption of $AgS_2O_3(aq)$ complexes. Assume that free Ag^+ and $S_2O_3^{2-}$ ions adsorb in the 'o' layer; that Na^+ and NO_3^- adsorb in the β layer, and that when $AgS_2O_3(aq)$ sorbs, the S_2O_3 portion of the molecule resides in the 'o' layer, but the Ag portion resides in the beta layer.

8. Figure 13.33 shows linearized fits to the Langmuir isotherm according to Equation 13.11 for sorption of Cd onto goethite (α-FeOOH) at pH 7.0 and various temperatures. Estimate the molar enthalpy of the adsorption reaction and predict the adsorption density of Cd in equilibrium with a dissolved concentration of $5 \times 10^{-5} M$ at 2°C.

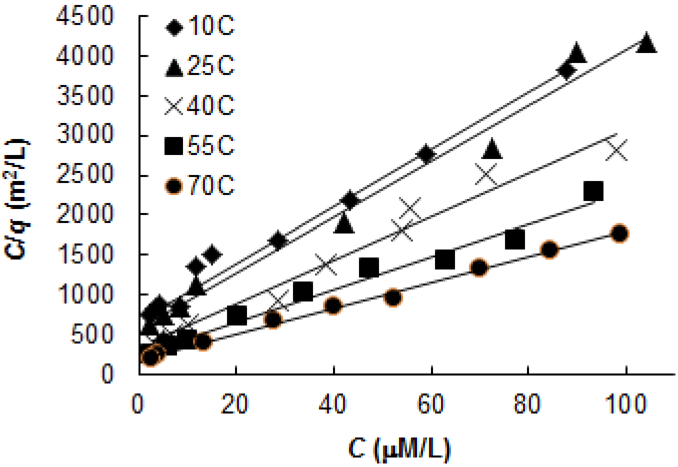

Figure 13.33. Linearized Langmuir isotherms for adsorption of Cd^{2+} onto goethite [after Johnson[10]].

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[10] Johnson, B.B. (1990) "Effect of pH, temperature, and concentration on the adsorption of cadmium on goethite." *Environ. Sci. Technol. 24*(1), 112-118.