Key for Unit I Exam

This exam consists of three shorter problems that call for written responses and/or shorter calculations, and three problems on the modeling of equilibrium systems.

Prepare your responses to each qeustion in the form of an organized and well-written narrative that explains how you approached the problem and that clearly states your conclusions. Where derivations and coding is involved, be sure to organize and annotate your work so that I can assign partial credit where appropriate. Neatness is a plus!

You are free to use your textbook, the library, web resources, previous problem sets, your notes, and handouts from class while working on this exam. You are not free to discuss any portion of this exam with other students or with faculty members other than the instructor. This restriction applies to R as well. Please direct all questions about the exam or about the use of R to the instructor.

A **_hard copy_** of your answers are due in class on Friday, March 15th.

Part I: Shorter Questions

Question 1 (8 points). One method for the quantitative analysis of magnesium is to precipitate it as $MgNH_4PO_4 \bullet 6H_2O$, isolate the precipitate by filtration, and convert it to $Mg_2P_2O_7$ by heating at high temperature. An interesting feature of $MgNH_4PO_4 \bullet 6H_2O$ is that it includes both a weak acid cation, NH_4^+, and a weak base anion, PO_4^{3-}. Draw ladder diagrams for NH_4^+ and PO_4^{3-}. Based on your ladder diagram, estimate the pH when you add $MgNH_4PO_4 \bullet 6H_2O$ to water. The pK_a value for NH_4^+ is 9.24 and the successive pK_a values for H_3PO_4 are 2.15, 7.20, and 12.35. Explain your reasoning in 1–3 sentence.

Answer. When we add $MgNH_4PO_4 \cdot 6\,H_2O(s)$ to water, it dissociates to an extent limited by its solubility reaction

$$MgNH_4PO_4 \cdot 6\,H_2O(s) \rightleftharpoons Mg^{2+}(aq) + NH_4^+(aq) + PO_4^{3-}(aq) + 6H_2O(l)$$
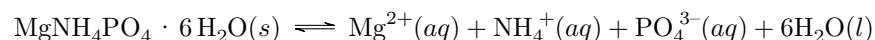
The ladder diagrams for NH_4^+ and for PO_4^{3-} are shown here.
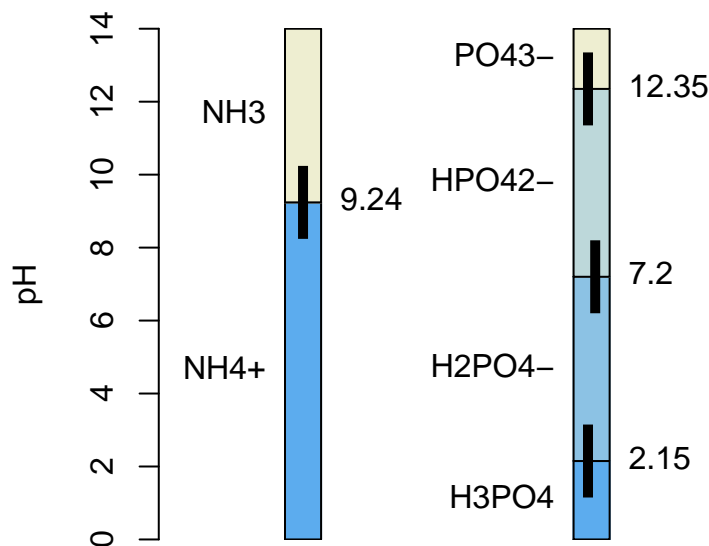
As the predominance regions for NH_4^+ and PO_4^{3-} do not overlap, the weak acid NH_4^+ will react stoichiometrically with the weak base PO_4^{3-} to form NH_3 and HPO_4^{2-}. A reasonable guess for the approximate pH is near the average of pK_2 and pK_3 for H_3PO_4, or a pH between 10.24 and 11.35.

Question 2 (9 points). Extreme halophile ("salt-loving") bacteria thrive in environments that are rich in dissolved salts, such as the Bonneville Salt Flats in Utah. To study these bacteria in lab, you must prepare a suitable medium that replicates their natural environment. A typical medium is prepared by diluting 250 g of NaCl, 5.0 g of KCl, 5.0 g of $MgCl_2 \bullet 6H_2O$, and 5.0 g of NH_4Cl to 700 mL with distilled water. What is the ionic strength of this solution to two significant figures?

Answer. To calculate the ionic strength, we first calculate the concentrations, C, of the salts in solution where

$$C = \frac{\text{mass/molar mass}}{\text{volume}}$$

salt	mass (g)	molar mass (g/mol)	concentration (M)
NaCl	250	58.44	6.11
KCl	5.0	74.55	0.0958
$MgCl_2 \cdot 6H_2O$	5.0	203.306	0.0351
NH_4Cl	5.0	53.492	0.134

Given the concentrations of the salts, the concentrations of the individual cations are $[Na^+] = 6.11$ M, $[K^+] = 0.0958$ M, $[Mg^{2+}] = 0.0351$ M, and $[NH_4^+] = 0.134$ M. To find the concentration of chloride, we simply add together its concentration from each salt, adjusting for stoichiometry in the case of $MgCl_2 \cdot 6H_2O$

$$[Cl^-] = 6.11 + 0.0958 + (2 \times 0.0351) + 0.134 = 6.41 \text{ M}$$

The ionic strength, therefore, is

$$\mu = \frac{1}{2}\sum (6.11)(+1)^2 + (0.0958)(+1)^2 + (0.0351)(+2)^2 + (0.134)(+1)^2 + (6.41)(-1)^2 = 6.45 \text{ M}$$

Question 3 (8 points). The extended Debeye-Hückel equation is given by the following equation

$$-\log\gamma_A = \frac{0.51 Z_A^2 \sqrt{\mu}}{1 + 3.3\alpha_A\sqrt{\mu}}$$

Using your ionic strength from Question 2, calculate water's concentration dissociation constant, K_w given that its thermodynamic dissociation constant is 1.00×10^{-14}, and knowing that α is 0.9 for H_3O^+ and 0.35 for OH^-. If you do not have an ionic strength from Question 2—or not confident that your ionic strength is reasonable—then assume an ionic strength of 0.40.

Answer. The relationship between the thermodynamic equilibrium constant of 1.00×10^{-14} and its concentration equilibrium constant, K_w, is

$$1.00 \times 10^{-14} = \gamma_{H_3O^+}[H_3O^+]\gamma_{OH^-}[OH^-] = K_w\gamma_{H_3O^+}\gamma_{OH^-}$$

To calculate K_w, we first must calculate the activity coefficients, γ, for H_3O^+ and for OH^-

$$-\log\gamma_{H_3O^+} = \frac{(0.51)(+1^2)\sqrt{6.45}}{1 + (3.3)(0.9)\sqrt{6.45}}$$

$$\gamma_{H_3O^+} = 0.705$$

$$-\log\gamma_{OH^-} = \frac{(0.51)(-1^2)\sqrt{6.45}}{1 + (3.3)(0.35)\sqrt{6.45}}$$

$$\gamma_{\text{OH}^-} = 0.468$$

$$K_{\text{w}} = \frac{1.00 \times 10^{-14}}{(0.705)(0.468)} = 3.03 \times 10^{-14}$$

If you use an ionic strength of 0.4, the activity coefficients are 0.773 for H_3O^+ and 0.651 for OH^-, and K_{w} is 1.99×10^{-14}.

Part II: Longer Questions

Problem 4 (25 points). In our second case study we modeled the adsorption of Pb^{2+} on aluminum oxide, $Al_2O_3(s)$, as a function of pH by accounting for the acid-base chemistry of the aluminum oxide surface

$$AlOH_2^+ + H_2O(l) \rightleftharpoons H_3O^+(aq) + AlOH \qquad K_{a1} = 1.0 \times 10^{-6} = \frac{[H_3O^+][AlOH]}{[AlOH_2^+]}$$

$$AlOH + H_2O(l) \rightleftharpoons H_3O^+(aq) + AlO^- \qquad K_{a2} = 2.0 \times 10^{-8} = \frac{[H_3O^+][AlO^-]}{[AlOH]}$$

the dissociation of water

$$2H_2O(aq) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

and the monodentate complexation of Pb^{2+} with a surface site

$$Pb^{2+}(aq) + AlO^- \rightleftharpoons AlOPb^+ \qquad K_1 = 1.23 \times 10^6 = \frac{[AlOPb^+]}{[Pb^{2+}][AlO^-]}$$
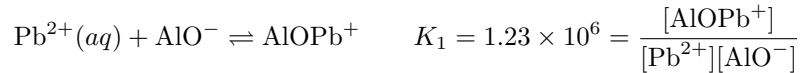
obtaining the result shown here when the total concentration of surface sites is 0.1 mM and the total concentration of lead is 0.1μM.
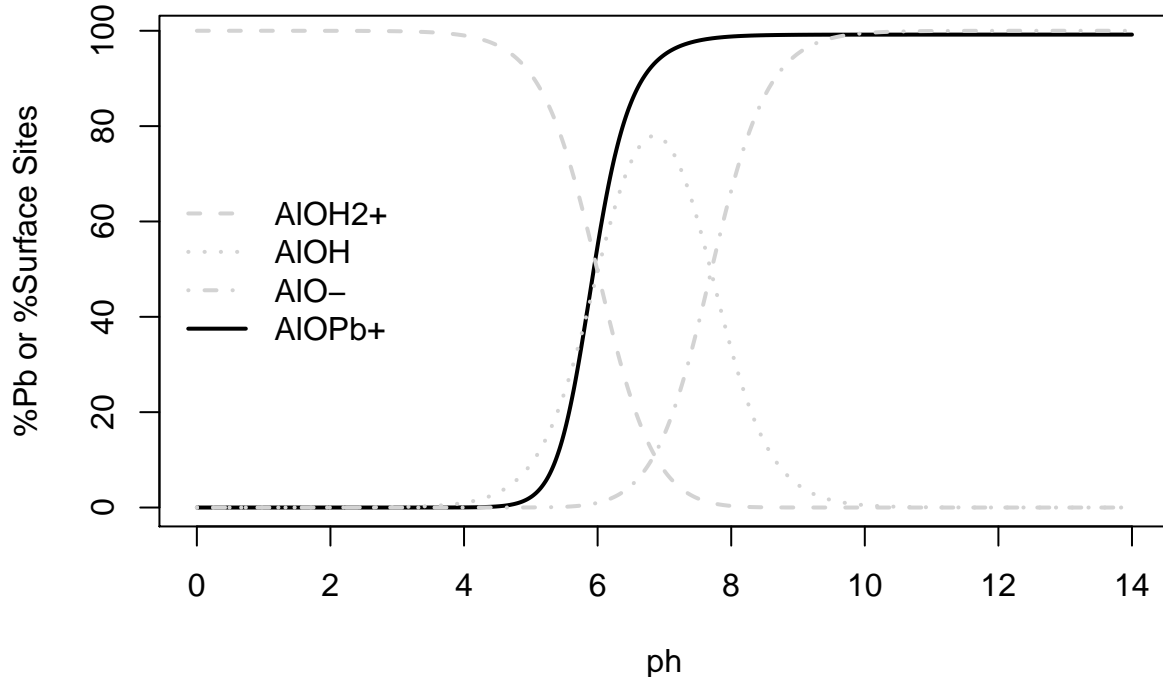
A more complete model of this system includes the formation of soluble $PbOH^+$ *(aq)*

$$Pb^{2+}(aq) + OH^-(aq) \rightleftharpoons PbOH^+(aq) \qquad K_{OH} = \frac{[PbOH^+]}{[Pb^{2+}][OH^-]} = 2.0 \times 10^6$$
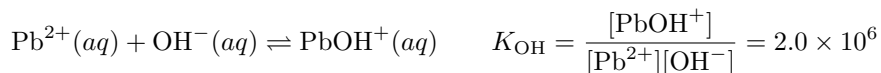
and the bidentate complexation of Pb^{2+} with a surface site

$$Pb^{2+}(aq) + 2AlO^- \rightleftharpoons (AlO)_2Pb \qquad \beta_2 = 7.9 \times 10^{10} = \frac{[(AlO)_2Pb]}{[Pb^{2+}][AlO^-]^2}$$
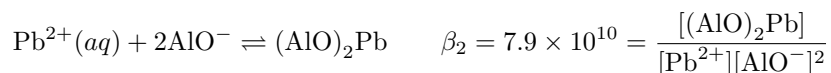
Beginning with the model we developed in class, modify it to include these two additional reactions. The code for our original model is available on the course's archive page as the R-script file PbAl203.R. Extend this code by adding equilibrium constants for the formation of $PbOH^+$ and $(AlO)_2Pb$, and by adding equations for the concentrations of $PbOH^+$ and $(AlO)_2Pb$ in terms of the concentration of uncomplexed Pb^{2+}. Create a single plot that shows the percentage of lead in the forms $PbOH^+$, $AlOPb^+$, $(AlO)_2Pb$, and total adsorbed lead—that is, the sum of $AlOPb^+$ and of $(AlO)_2Pb$—as a function of pH.

After you modify the R script, save it using the file name PbAl2O3_yourlastname.RR and compile the code as a pdf (preferred) or an html notebook (if necessary). Turn in a copy of your notebook, a brief explanation of how you arrived at your equations for the concentration of $(AlO)_2Pb$ and of $PbOH^+$, and a brief discussion of your observations of the similarities and differences between the original, simplified model and this more complete model. In addition, send me a copy of your modified script by email.

Answer. The modified code and its output are shown below. In addition to adding the formation constants for $(AlO)_2Pb$ and for $PbOH^+$, identified as Kalo2pb and Kpboh, respectively, equations for both species are added to the section that defines the concentrations of lead species; these equations are

$$[(AlO)_2Pb] = K_{(AlO)_2Pb} \times [AlO^-]^2 \times [Pb^{2+}]$$

$$[PbOH^+] = K_{PbOH^+} \times [OH^-] \times [Pb^{2+}]$$

To derive equations for the concentrations of the species, we begin with a mass balance on Pb^{2+}

$$C_{Pb} = [Pb^{2+}] + [AlOPb^-] + [(AlO)_2Pb] + [PbOH^+]$$

which gives

$$[Pb^{2+}] = \frac{C_{Pb}}{1 + K_1[AlO^-] + \beta_2[AlO^-]^2 + K_{OH}[OH-]}$$

There are two notable features of this plot. First, for high pH values the lead desorbs from the surface to form the soluble $PbOH^+$ metal–ligand complex; this is not surprising as the concentration of OH^- becomes significant above a pH of 10. Second, at pH levels that favor the formation of fully deprotonated surface sites (i.e. AlO^-), lead adsorbs onto the surface primarily through bidentate (i.e. $(AlO)_2Pb$) complexation.

```
# acid dissociation constants for surface sites
Ka1 = 1.00e-6
Ka2 = 2.00e-8
Kw = 1.00e-14

# complexation constants for lead
Kalopb = 1.23e6
Kalo2pb = 7.9e10
Kpboh = 2e6

# mass balances
Caloh = 1e-4
Cpb = 1e-7
```

4

```r
# set up master variable
ph = seq(0, 14, 0.01)

# calculate concentrations of hydronium and hydroxide ions
h = 10^-ph
oh = Kw/h

# calculate concentrations of surface sites
aloh2 = Caloh/(1 + Ka1/h + Ka1*Ka2/h^2)
aloh = Ka1*aloh2/h
alo = Ka1*Ka2*aloh2/h^2

# calculate concentrations of lead
pb = Cpb/(1 + Kalopb*alo + Kalo2pb*alo^2 + Kpboh*oh)
alopb = Kalopb*alo*pb
alo2pb = Kalo2pb*alo^2*pb
pboh = Kpboh*oh*pb

# plot the results for lead
plot(ph, 100*alopb/Cpb, type = "l", lty = 1, lwd = 2, xlim = c(0, 14),
     ylim = c(0, 100), ylab = "%Pb or %Surface Sites", xlab = "pH")
lines(ph, 100*alo2pb/Cpb, lty = 2, lwd = 2)
lines(ph, 100*pboh/Cpb, lty = 3, lwd = 2)
lines(ph, 100*(alopb + alo2pb)/Cpb, lty = 4, lwd = 2)

# overlay the results for the surface sites
lines(ph, 100*aloh2/Caloh, col = "lightgray", lty = 2, lwd = 2)
lines(ph, 100*aloh/Caloh, col = "lightgray", lty = 3, lwd = 2)
lines(ph, 100*alo/Caloh, col = "lightgray", lty = 4, lwd = 2)

# add a legend
legend(x = "left",
       legend = c("PbOH+", "AlOPb+", "(AlO)2Pb", "AlOPb+ & (AlO)2Pb"),
       lwd = c(2, 2, 2, 2), lty = c(3, 1, 2, 4), bty = "n")
```
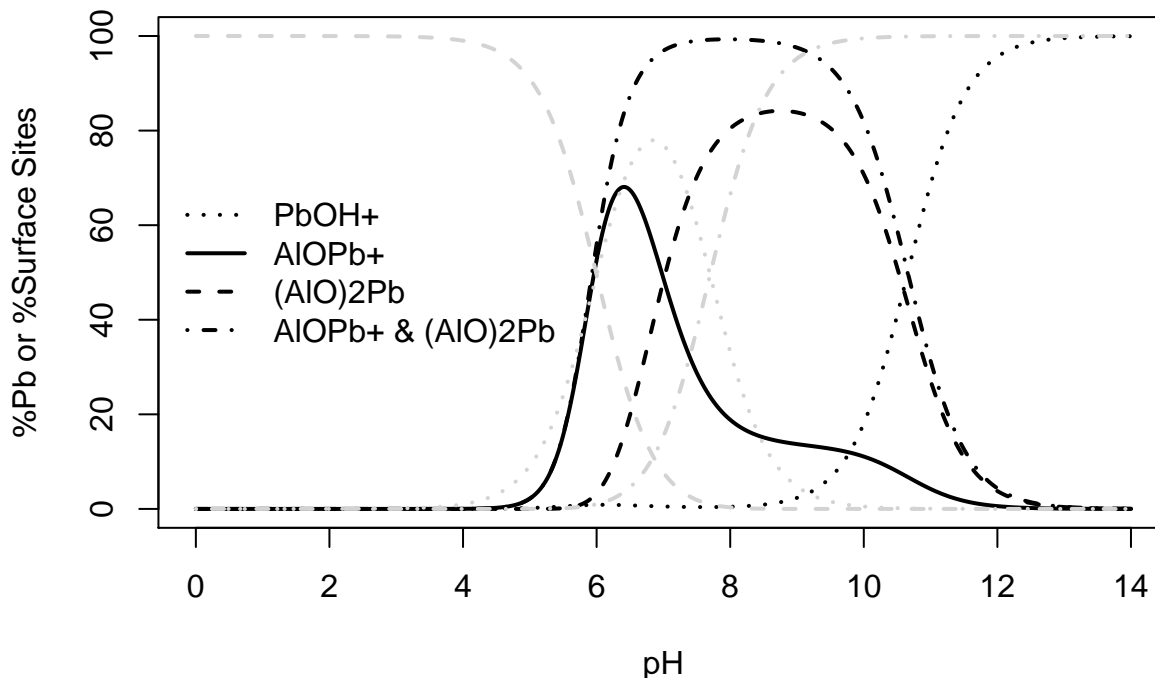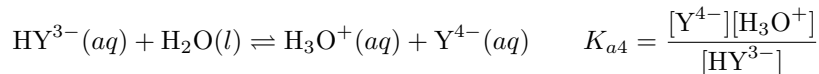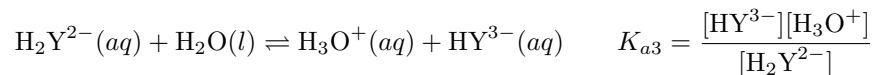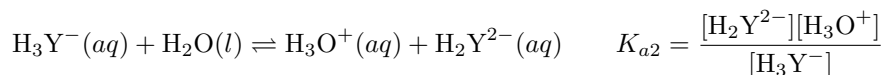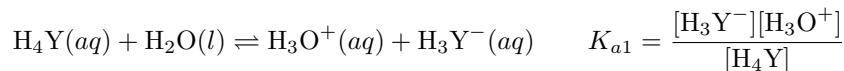
Problem 5 (25 points). Ethylenediaminetetracetic acid, EDTA, is ligand that forms strong complexes with divalent and trivalent metal ions. Although EDTA is a hexaprotic acid, the equilibrium modeling of its acid-base chemistry typically considers only its last four acid dissociation reactions

$$H_4Y(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_3Y^-(aq) \qquad K_{a1} = \frac{[H_3Y^-][H_3O^+]}{[H_4Y]}$$

$$H_3Y^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2Y^{2-}(aq) \qquad K_{a2} = \frac{[H_2Y^{2-}][H_3O^+]}{[H_3Y^-]}$$

$$H_2Y^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HY^{3-}(aq) \qquad K_{a3} = \frac{[HY^{3-}][H_3O^+]}{[H_2Y^{2-}]}$$

$$HY^{3-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Y^{4-}(aq) \qquad K_{a4} = \frac{[Y^{4-}][H_3O^+]}{[HY^{3-}]}$$

where Y^{4-} is the fully deprotonted form of EDTA. The successive pK_a values are 2.00, 2.66, 6.16, and 10.24.

Build a mathematical model of EDTA's acid–base chemistry and use your model to create a distribution diagram that shows the log10(concentration) of EDTA present in each of its forms as a function of pH. Assume that the concentration of EDTA is 0.0010 M. Which form of EDTA is most important in the following media: blood (7.35 < pH < 7.45), seawater (pH = 8.2), and acid-mine drainage (pH < 3.5)?

The binding of EDTA with a metal ion is called chelation. One method for reducing the concentration of Pb^{2+} in blood following lead poisoning, is to administer EDTA intravenously. Modify your model from above to include the complexation of Pb^{2+} by EDTA

$$Pb^{2+}(aq) + Y^{4-}(aq) \rightleftharpoons PbY^{2-}(aq) \qquad K_1 = \frac{[PbY^{2-}]}{[Pb^{2+}][Y^{4-}]}$$
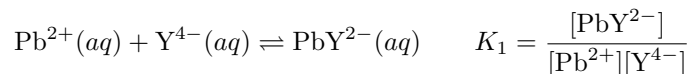
assuming a total analytical concentration of Pb^{2+} of $1.0\mu M$ and knowing that $logK_1$ is 18.04. Based on your model, what is the concentration of uncomplexed Pb^{2+} at blood pH of 7.40?

Use the template EDTA.R to build your model, placing values in the appropriate sections. Save the file using the file name EDTA_yourlastname.R and compile the code as a pdf (preferred) or an html notebook (if

necessary). Turn in a copy of your notebook, a brief explanation showing how you arrived at your equations for the concentration of the EDTA and Pb species, and how you determined the concentration of uncomplexed Pb^{2+} in blood. In addition, send me a copy of your modified script by email.

Answer. The code and its output are shown below based on a mass balance for Pb^{2+} of

$$C_{Pb} = [Pb^{2+}] + [PbY_2^-]$$

The concentration of uncomplexed Pb^{2+} is 6.68×10^{-20} M, which is a dramatic reduction from its original concentration of $1.0\mu M$, which explains why EDTA is an effective treatment for lead poisoning.

```r
# edta equilibrium constants
ka1 = 10^-2
ka2 = 10^-2.66
ka3 = 10^-6.16
ka4 = 10^-10.24

# mass balance on edta
Cedta = 0.0010

# water dissociation
kw = 10^-14

# master variable
ph = seq(0, 14, 0.01)

# concentration of H3O+ and OH-
h = 10^-ph
oh = kw/h

# concentration of edta species
h4y = Cedta/(1 + ka1/h + ka1*ka2/h^2 + ka1*ka2*ka3/h^3 + ka1*ka2*ka3*ka4/h^4 )
h3y = h4y*ka1/h
h2y = h4y*ka1*ka2/h^2
hy = h4y*ka1*ka2*ka3/h^3
y = h4y*ka1*ka2*ka3*ka4/h^4

# equilibrium constants for metals
Kpby = 10^18.04

# mass balance concentrations for metals
Cpb = 1e-6

# equations for concentrations of metals
pb = Cpb/(1 + Kpby*y)
pby = Kpby*y*pb

# plot edta in gray
plot(ph,log10(h4y), type = "l", lty = 2, ylim = c(-24, -2), col = "gray",
     xlab = "pH", ylab = "log10(concentration)",
     panel.first = rect(c(7.35), -30, c(7.45), -1, col = "tan", border = NA))
lines(ph, log10(h3y), lty = 3, col = "gray")
lines(ph, log10(h2y), lty = 4, col = "gray")
lines(ph, log10(hy), lty = 5, col = "gray")
lines(ph, log10(y), lty = 6, col = "gray")
text(x = c(7.4), y = c(-5), srt = 90, labels = c("blood"))
```
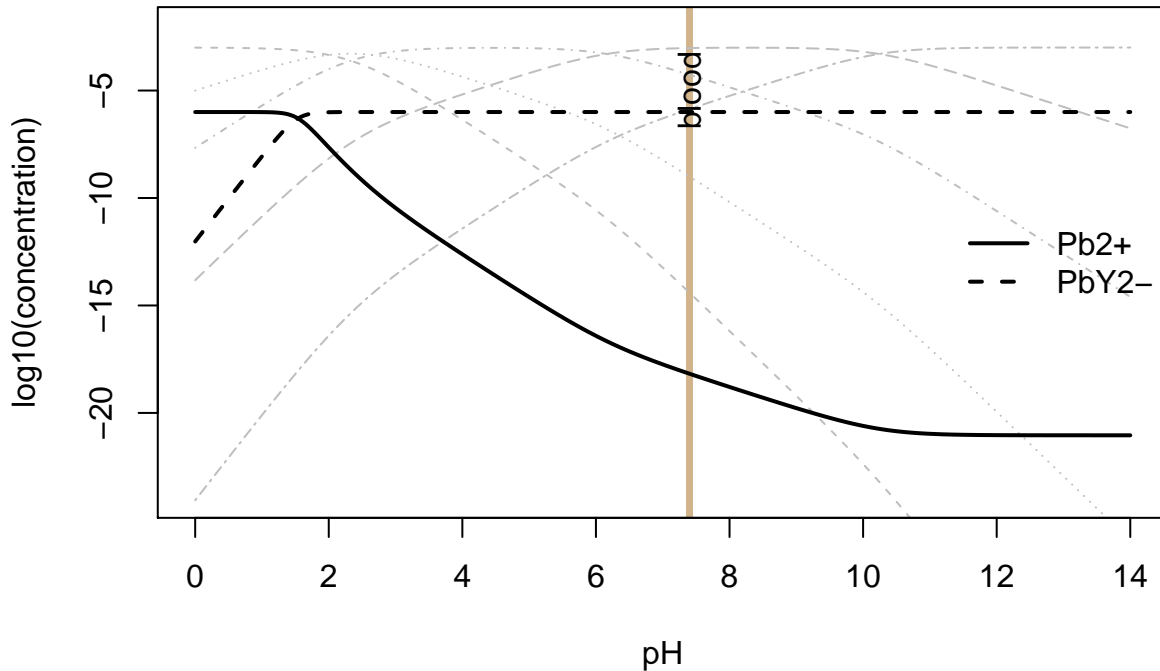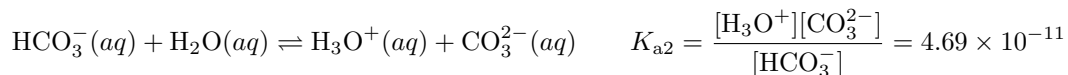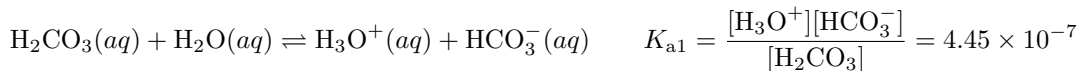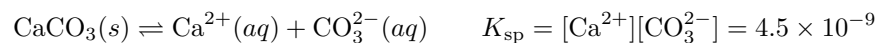
```
# plot metals
lines(ph, log10(pb), lty = 1, lwd = 2)
lines(ph, log10(pby), lty = 2, lwd = 2)
legend(x = "right",
       legend = c("Pb2+", "PbY2-"),
       lty = c(1, 2), lwd = c(2,2), bty = "n")
```



```
# return concentration of lead at pH of blood
id = which(ph == 7.4)
pb[id]
```

```
## [1] 6.681778e-19
```

Problem 6 (25 points). Calcium carbonate, $CaCO_3$, is an important component of our natural environment. It accounts for 4-5% of the earth's crust, primarily in the form of chalk, limestone, and marble, and plays an important role in the chemistry of the oceans, particularly as a sink for atmospheric CO_2, and in the chemistry of cave formation. Develop a model for the solubility of $CaCO_3$ as a function of pH based on the following set of equilibrium reactions

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.5 \times 10^{-9}$$

$$H_2CO_3(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad K_{a1} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7}$$

$$HCO_3^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

Present the results of your model as a plot of log10(solubility), over the range -10 to 4, as a function of pH. Add lines to your plot that show the log10(concentrations) of H_2CO_3, HCO_3^-, and CO_3^{2-}.

Use the template Carbonate.R to build your models, placing values in the appropriate sections. Save the file using the file name Carbonate_yourlastname.R and compile the code as a pdf (preferred) or an html notebook (if necessary). Turn in a copy of your notebook, a brief explanation showing how you arrived at your equations for the solubility of $CaCO_3$ and for the concentration of the carbonate species. In addition, send me a copy of your modified script by email.

Answer. The code and output are shown below based on a mass balance equation of

$$[\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$$

and solving for three of the species in terms of the fourth; the code below, for example, defines the concentration of HCO_3^- as

$$[\text{HCO}_3^-] = \sqrt{\frac{K_{\text{sp}}[\text{H}_3\text{O}^+]/K_{\text{a2}}}{K_{\text{a2}}/[\text{H}_3\text{O}^+] + 1 + [\text{H}_3\text{O}^+]/K_{\text{a1}}}}$$

Note that, as expected, solubility is lowest under more basic pH levels where CO_3^{2-} is the dominate form of carbonate, and greatest at more acidic pH levels where H_2CO_3 is the dominate form of carbonate.

```r
# equilibrium constants for carbonate
Ka1 = 4.45e-7
Ka2 = 4.69e-11
Ksp = 4.5e-9

# equilibrium constant for water
kw = 1.00e-14

# set up master variable
ph = seq(0, 14, 0.01)

# concentrations of hydronium and hydroxide
h = 10^-ph
oh = kw/h

# concentrations of carbonate species
hco3 = sqrt((Ksp*h/Ka2)*(Ka2/h + 1 + h/Ka1)^-1)
co3 = Ka2*hco3/h
h2co3 = h*hco3/Ka1

# solubility
sol = co3 + hco3 + h2co3

# plot
plot(ph, log10(sol), type = "l",
     ylim = c(-10, 4), xlab = "pH",
     ylab = "log10(solubility) or log10(conc)", lwd = 2)
lines(ph, log10(h2co3), lty = 2)
lines(ph, log10(hco3), lty = 3)
lines(ph, log10(co3), lty = 4)
legend(x = "topright",
       legend = c("solubility", "H2CO3", "HCO3-", "CO32-"),
       lty = c(1, 2, 3, 4), lwd = c(2, 1, 1, 1), bty = "n")
```
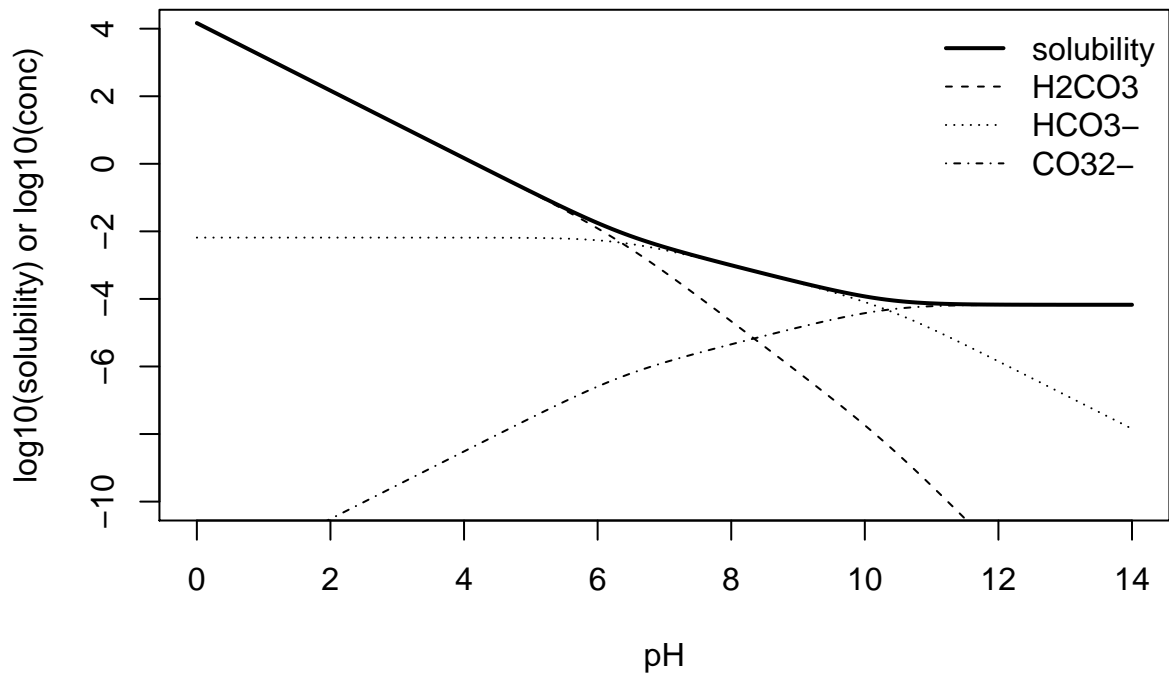
Note: The code from examples discussed in class provides examples of how to use the plot(), lines(), and legend() commands to create an initial plot, to overlay new data onto an existing plot, and to add a legend to a plot. If you cannot figure out how to write code to create a particular plot that meets your needs, then please feel free to ask.