Due: Friday, 10/3 by 5 p.m.

Solutions will be posted on the Web. Problem sets will be graded for completeness, and one problem (selected at random) will be graded in detail. Each problem set contributes 2.5% towards your final grade.

1. Problem 6.8, p. 118 in the text.
   NaHCO₃ is added to water. Generate a species list diagram for this system.

   SOLUTION:
   We must first define the system. Here it will be defined as closed, and the amount of NaHCO₃ added is small enough that it will all dissolve.

   Starting components: NaHCO₃(s) H₂O

   Na⁺ HCO₃⁻ H⁺ OH⁻

   CO₃²⁻ H₂CO₃

2. Problem 6.9, p. 118 in the text.
   Write a complete mathematical model for the system above. The system is closed, and all NaHCO₃(s) dissolves.

   SOLUTION:
   1. Define system: closed; all bicarbonate dissolves
   2. List species (see above)
      a. H₂O, H⁺, OH⁻, Na⁺, HCO₃⁻, CO₃²⁻, H₂CO₃ (7)
   3. Identify 7 equations for the system
      a. Kw = {H⁺}{OH⁻}/{H₂O(l)}
      b. K₁ = {HCO₃⁻}{H⁺}/{H₂CO₃}
      c. K₂ = {CO₃²⁻}{H⁺}/{HCO₃⁻}
      d. C_T = [Na⁺]
      e. C_T = [H₂CO₃] + [HCO₃⁻] + [CO₃²⁻]
      f. [H⁺] + [Na⁺] = [OH⁻] + [HCO₃⁻] + [CO₃²⁻]
      g. {H₂O(l)} = 1
3. If you wanted to predict the pH of rain water in which you had found Ca\(^{2+}\), Na\(^{+}\), Cl\(^{-}\), HCO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\), and NO\(_3\)\(^{-}\), list the chemical species you would consider and the equations that you would use to solve for the pH.

**SOLUTION:**

1. Define the system: closed (rain sample has been collected and bottled)
2. List species:
   a. Starting substances: H\(_2\)O, Ca\(^{2+}\), Na\(^{+}\), Cl\(^{-}\), HCO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\), NO\(_3\)\(^{-}\)
   b. Initial hydrolysis: H\(^+\), OH\(^-\), H\(_2\)CO\(_3\), CO\(_3\)\(^{2-}\), HSO\(_4\)\(^{-}\), HNO\(_3\), HCl
   c. Further hydrolysis H\(_2\)SO\(_4\), NaHCO\(_3\), NaCO\(_3\)\(^{-}\), NaSO\(_4\)\(^{-}\), CaOH\(^{+}\), CaHCO\(_3\)\(^{+}\), CaCO\(_3\)

   The total above is 23. However, HCl, H\(_2\)SO\(_4\) and HNO\(_3\) are strong acids that dissociate nearly completely; the concentrations of these species will be vanishingly small. This leaves us with 20 unknowns for which we need 20 equations.

   1. \(K_w = [H^+] \times [OH^-]/[H_2O]\)
   2. \(K_1 = [H^+] \times [HCO_3^-]/[H_2CO_3]\)
   3. \(K_2 = [H^+] \times [CO_3^{2-}]/[HCO_3^-]\)
   4. \(K_{a2} = [H^+] \times [SO_4^{2-}]/[HSO_4^-]\)
   5. \(K_{f1} = [CaHCO_3^{+}]/[Ca^{2+}] \times [HCO_3^-]\)
   6. \(K_{NaHCO3} = [NaHCO_3]/[Na^+] \times [HCO_3^-]\)
   7. \(K_{NaCO3} = [NaCO_3^-]/[Na^+] \times [CO_3^{2-}]\)
   8. \(K_{NaSO4} = [NaSO_4^-]/[Na^+] \times [SO_4^{2-}]\)
   9. \(K_{CaOH} = [CaOH^+] \times [Ca^{2+}]/[OH^-]\)
   10. \(K_{CaCO3} = [CaCO_3]/[Ca^{2+}] \times [CO_3^{2-}]\)
   11. \(K_{CaCl} = [CaCl^+]/[Ca^{2+}] \times [Cl^-]\)
   12. \(K_{CaSO4} = [CaSO_4^-]/[Ca^{2+}] \times [SO_4^{2-}]\)
   13. \(C_{T-Ca} = [Ca^{2+}] + [CaHCO_3^+] + [CaCO_3] + [CaCl^+] + [CaSO_4]\)
   14. \(C_{T-Na} = [Na^+] + [NaHCO_3] + [NaCO_3^-] + [NaSO_4^-]\)
   15. \(C_{T-Cl} = [Cl^-] + [CaCl^+]\)
   16. \(C_{T-S} = [HSO_4^-] + [SO_4^{2-}] + [CaSO_4] + [NaSO_4]\)
   17. \(C_{T-N} = [NO_3^-]\)
   18. \(C_{T-C} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] + [CaHCO_3^+] + [CaCO_3] + [NaHCO_3] + [NaCO_3]\)
   19. \([H^+] + 2[Ca^{2+}] + [Na^+] + [CaHCO_3^+] + [CaCO_3] + [CaCl^+] = [OH^-] + [Cl^-] + [NO_3^-] + 2[SO_4^{2-}] + [HSO_4^-] + [HCO_3^-] + 2[CO_3^{2-}] + [NaCO_3] + [NaSO_4^-]\)
   20. \([H_2O] = 1\)

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At 30\(^\circ\)C, \(K_w = 10^{-13.83}\). Determine the equilibrium pH of pure water at this temperature.

**SOLUTION:**

\(K_w = [H^+] \times [OH^-]/[H_2O] = [H^+] \times [OH^-]\)

In pure water, \([H^+] = [OH^-]\)
\[ K_w = \{H^+\}^2 = 10^{-13.83} \]
\[ \Rightarrow \{H^+\} = 10^{-6.92} \]
\[ \Rightarrow \text{pH} = 6.92 \]

5. Problem 7.12, p. 139 in the text.
Find the equilibrium pH of orange juice when only the first dissociation of citric acid is considered. (Ignore activity corrections)

**SOLUTION:**
1. System is closed with no solids present.
2. Identify components and species:
   \( H_3C, K^+, H^+, OH^-, H_2C^- \) (5 species) Assume \( K_3C, K_2HC, KH_2C, KC^- \) etc. are unimportant if present.
3. Identify constraints (5 equations)
   a. \( K_w = \{H^+\}\{OH^-\} = 10^{-14} \)
   b. \( K_{a1} = \{H^+\} \{H_2C^-\}/\{H_3C\} = 10^{-3.14} \)
   c. \( CT_{-\text{citrate}} = [H_2C^-] + [H_3C] = (8 \text{ g/L})/(192 \text{ g/mole}) = 0.042 \text{ M} = 10^{-1.38} \text{ M} \)
   d. \( CT_{-K} = [K^+] = (1.6 \text{ g/L})/(39 \text{ g/mole}) = 0.041 \text{ M} = 10^{-1.39} \text{ M} \)
   e. [\( H^+ \] + [\( K^+ \] = [\( OH^- \] + [\( H_2C^- \]
4. Solve
   a. Assume solution is acidic so \( OH^- \) is negligible in charge balance
      \[ [H_2C^-] = [H^+] + [K^+] \]
      \[ [H_3C] = CT_{-\text{citrate}} - [H_2C^-] = CT_{-\text{citrate}} - [H^+] - CT_{-K} = 0.001 - [H^+] \]
      \( K_{a1} = \{H^+\}(\{H^+\} + 0.041)/(0.001-\{H^+\}) \)
      \[ 0.001K_{a1} - K_{a1}\{H^+\} = \{H^+\}^2 + 0.041\{H^+\} \]
      \[ \{H^+\}^2 + (0.041+K_{a1})\{H^+\} - 0.001K_{a1} = 0 \]
      \[ \{H^+\} = \frac{-0.04175 + (0.04175^2 - 4(0.001\times10^{-6.14})^{1/2}}{2} \]
      \[ \{H^+\} = 10^{-4.76} \Rightarrow \text{pH} = 4.76 \]

Find the equilibrium pH of a \( 10^{-3} \text{ M} \) NaCN solution using graphical means.

**SOLUTION:**
\( K_a = \{H^+\}\{CN^-\}/\{HCN\} = 10^{-9.2} \) or \( pK_a = 9.2 \)
\( \{CN^-\} = K_a CT/(\{H^+\] + K_a) \)
Given the proton condition: \([\text{HCN}] + [\text{H}^+] = [\text{OH}^-]\)
The solution must be where the HCN line crosses the OH\(^-\) line at pH ~ 10.2.

The charge balance equation \(([\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{CN}^-])\) has no single solution point.

7. Problem 8.8, p. 169 in the text.
Write proton conditions.
A. \(\text{NH}_4\text{Cl}\)

Solution: The proton reference level is \(\text{NH}_4^+, \text{Cl}^-\) and \(\text{H}_2\text{O}\)
Species with more protons: \(\text{HCl}, \text{H}^+\)
Species with fewer protons: \(\text{NH}_3, \text{OH}^-\)
Proton Condition: \([\text{HCl}] + [\text{H}^+] = [\text{NH}_3] + [\text{OH}^-]\)

B. \(\text{Na}_2\text{S}\)
Solution: The proton reference level is \(\text{Na}^+, \text{S}^{2-}, \text{H}_2\text{O}\)
Species with two more protons: \(\text{H}_2\text{S}\)
Species with one more proton: \(\text{HS}^-, \text{H}^+\)
Species with fewer protons: \(\text{OH}^-\)
Proton Condition: \(2[\text{H}_2\text{S}] + [\text{HS}^-] + [\text{H}^+] = [\text{OH}^-]\)
C. $\text{KH}_2\text{PO}_4$

Solution: The proton reference level is $\text{K}^+, \text{H}_2\text{PO}_4^-, \text{H}_2\text{O}$

Species with one more proton: $\text{H}_3\text{PO}_4, \text{H}^+$
Species with one less proton: $\text{HPO}_4^{2-}, \text{OH}^-$
Species with two fewer protons: $\text{PO}_4^{3-}$

Proton Condition: $[\text{H}_3\text{PO}_4] + [\text{H}^+] = [\text{HPO}_4^{2-}] + [\text{OH}^-] + 2[\text{PO}_4^{3-}]$

D. $(\text{NH}_4)_2\text{CO}_3$

Solution: The proton reference level is $\text{NH}_4^+, \text{CO}_3^{2-}, \text{H}_2\text{O}$

Species with two more protons: $\text{H}_2\text{CO}_3$
Species with one more proton: $\text{HCO}_3^-, \text{H}^+$
Species with one less proton: $\text{NH}_3, \text{OH}^-$

Proton Condition: $2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{H}^+] = [\text{NH}_3] + [\text{OH}^-]$

8. Problem 18.5, p. 414 in the text.
The MCL for chloroform in drinking water is 100 μg/L. The occupational exposure level for chloroform in air is 10 ppm by weight ($2.54 \times 10^{-6}$ atm). If treated water in an enclosed drinking water reservoir is at the MCL for chloroform, is the OEL for chloroform in air exceeded? Assume that the air volume of the enclosed reservoir is very large.

SOLUTION:
We are asked to find the concentration of chloroform in air that will be in equilibrium with 100 μg/L in water.

\[
\text{CHCl}_3(g) \leftrightarrow \text{CHCl}_3(aq) \quad K_H = 10^{-0.6} \text{ mole/L-atm}
\]

M.W. = $12 + 1 + 3 \cdot 35.5 = 199.5$

\[
(100 \mu\text{g/L})/(199.5 \mu\text{g/μmole}) = 0.837 \mu\text{M}
\]

\[
[\text{CHCl}_3(g)] = [\text{CHCl}_3(aq)]/K_H = (0.837 \times 10^{-6} \text{ mole/L})/(10^{-0.6} \text{ mole/L-atm})
\]

\[
[\text{CHCl}_3(g)] = 3.33 \times 10^{-6} \text{ atm}
\]

This value is higher than the OEL of $2.54 \times 10^{-6}$ atm

A ground water containing 0.5 mg/L as S of total dissolved sulfide at pH 7.5 is aerated to volatilize $\text{H}_2\text{S}$. If the $\text{H}_2\text{S}$ concentration in the atmosphere in contact with the aerated ground water is 0.75 ppm by volume and the total system pressure is 1 atm, what will be the total sulfide concentration in the water after equilibrium has been reached? Assume the pH of the water remains constant.

SOLUTION:
First, convert the mixing ratio to a concentration in atm.
\[ V_i = \frac{p_i}{P} \]
\[ \frac{0.75}{10^6} = \frac{p_i}{1\text{ atm}} \]
\[ p_i = 7.5 \times 10^{-7} \]

Next, use Henry's Law constant to calculate the equilibrium concentration of \( H_2S_{\text{aq}} \).

\[ K_H = 10^{-1.01} \frac{\text{mol}}{L \cdot \text{atm}} = \frac{[H_2S]_{\text{aq}}}{pH_2S} \]

\[ [H_2S]_{\text{aq}} = K_H \cdot pH_2S = 10^{-1.01} \frac{\text{mole}}{L \cdot \text{atm}} \cdot 7.5 \times 10^{-7} \text{ atm} \]

\[ [H_2S]_{\text{aq}} = 7.3 \times 10^{-8} \frac{\text{mol}}{L} \]

This, however, is not the total concentration of reduced sulfur. We also need to calculate the amount present as \( HS^- \).

\[ K_a = \frac{\{H^+\} \{HS^-\}}{[H_2S]_{\text{aq}}} = 10^{-7} \]

\[ \{HS^-\} = K_a \frac{[H_2S]_{\text{aq}}}{\{H^+\}} = 10^{-7} \cdot \frac{7.3 \times 10^{-8}}{10^{-7.5}} \]

\[ \{HS^-\} = 2.4 \times 10^{-7} \]

\[ S_{\text{total}} = [H_2S] + [HS^-] \]

\[ S_{\text{total}} = (0.73 + 2.4) \times 10^{-7} = 3.13 \times 10^{-7} \frac{\text{mole}}{L} \]

![Graph of pH vs. pOH]

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OH  
H  
H2S  
HS-  
pH
The pC-pH diagram can also be used to determine the results. Because the gas phase H₂S concentration is fixed, the concentration of H₂Sₐq will also remain fixed and independent of pH. Thus the H₂S line is horizontal. The line for HS⁻ will intersect the H₂S line at the pKₐ (both components have equal concentration at that pH), and it will have a slope of minus 1. We are told to find the concentrations at pH = 7.5, the vertical line on the graph.

10. a. If the alkalinity of the wastewater treatment sample that you have worked with in the lab is 2.5 meq/L, what must the pCO₂ in the sample be to cause the measured pH of 6.65?
   b. If the sample is equilibrated with room air (pCO₂ = 400 μatm), what will be the resultant pH? Include a pC-pH diagram with your solution of this problem; you may either use the diagram to solve the problem, or simply to depict the situation.

SOLUTION:
   a. Species present: H₂O, H⁺, OH⁻, CO₂(g), H₂CO₃⁺, HCO₃⁻, CO₃²⁻ (6)
   b. Equations: Kₐ = \{H⁺\} \{H₂CO₃⁺\}/\{H₂CO₃\} = 10⁻¹.₄₆
   Kₐ₁ = \{H⁺\} \{HCO₃⁻\}/\{H₂CO₃⁺\} = 10⁻₆.₂₅
   Kₐ₂ = \{H⁺\} \{CO₃²⁻\}/\{HCO₃⁻\} = 10⁻₁₀.₃
   pH = 6.65
   \[\text{HCO}_₃⁻\] = 2.5x10⁻³ mol/L
   c. Rearranging to solve:
   \[\text{pH} = \frac{\{\text{H}⁺\}}{\{\text{OH}⁻\}}\]
   \[\text{pCO}_₂(g) = \frac{\{\text{CO}_₂(aq)\}}{\text{K}_H} = \frac{\{\text{H}_₂\text{CO}_₃⁺\}}{\{\text{H}_₂\text{CO}_₃\}} = 10⁻¹.₄₆(2.5x10⁻³)^\gamma \]
   If I ~ 5 mM, then \[\gamma = 10^{\frac{-0.5\times0.005}{1+0.005}} = 0.927\]
   \[\{\text{H}_₂\text{CO}_₃⁺\} = \frac{\{\text{H}_₂\text{CO}_₃\}}{\{\text{CO}_₂(aq)\}} = (10⁻₆.₀₅)(2.5x10⁻³)0.927/10⁻₁.₄₆ = 9.2x10⁻⁴ \text{ M}\]
   pCO₂(g) = (9.2x10⁻⁴ M)/10⁻¹.₄₆ = 0.0266 atm = 26.6 matm

For the second question, let’s use a pC-pH diagram. This will be an open system with pCO₂ = 400 μatm. From the Kₐ equation, we can solve for H₂CO₃⁺ = 10⁻¹.₄₆(400×10⁻⁶atm) = 1.39x10⁻⁵ M
   Or pHH₂CO₃ = 4.86
   \[\{\text{HCO}_₃⁻\} = \text{K}_a₁ \{\text{H}_₂\text{CO}_₃⁺\}/\{\text{H}⁺\} \text{ or } \text{pHCO}_₃ = \text{pK}_a₁ + \text{pH}_H₂\text{CO}_₃⁺ - \text{pH} = 6.2₅+4.₈₆ - \text{pH} = 11.₁₁ - \text{pH}\]
   \[\{\text{CO}_₃²⁻\} = \text{K}_a₂ \{\text{HCO}_₃⁻\}/\{\text{H}⁺\} \text{ or } \text{pCO}_₃ = \text{pK}_a₂ + \text{pH}_\text{HCO}_₃⁻ - \text{pH}\]
The proton reference level is $\text{HCO}_3^-$, $\text{H}_2\text{O}$ so the proton condition is:

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

This equation is satisfied at the position of the circle, approximately pH 8.5.