Chapter 15 - Applications of Aqueous Equilibria

Neutralization Reactions

- Predict whether the pH after neutralization will be greater than, less than, or equal to 7 for the following combinations:
- HNO_2 and KOH
- HCl and LiOH
- HBr and NH_3

Neutralization Reactions

- Strong acid-strong base
  - $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
  - What's in solution? i.e. look at the net ionic equation
- Weak acid-strong base
  - $HA_{(aq)} + NaOH_{(aq)} \rightarrow NaA_{(aq)} + H_2O_{(l)}$
  - What's in solution? i.e. net ionic equation
  - What will the pH be, roughly?
  - Example: Acetic acid and sodium hydroxide

The Common Ion Effect

- Metal ions or salts containing a conjugate weak acid or base can shift the pH of a solution.
- This is the mechanism that controls the pH of your blood and other biological systems.

Neutralization Reactions

- Strong acid-weak base
  - $HCl_{(aq)} + NH_{3\,(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$
  - What's in solution?
  - What will the pH be, roughly?
- Weak acid-weak base
  - $CH_3COOH_{(aq)} + NH_{3\,(aq)} \leftrightarrow NH_4^+{}_{(aq)} + CH_3COO^-{}_{(aq)}$
  - Larger K values than other combinations
  - Reaction does not proceed as far toward completion as previous 3 reactions.

The Common Ion Effect

- If we add a conjugate acid (base) to a solution of a weak base (acid), the pH will shift. This is called the **Common Ion Effect**.
- $NaCH_3CO_2$ added to a solution of CH_3CO_2H will make the solution more basic. Why?
- A common ion will shift a chemical equilibrium in such a direction as to get rid of some of the added ion. (think Le Chatelier's principle)

Common Ion Effect

- $CH_3CO_2H + H_2O \leftrightarrow CH_3CO_2^- + H_3O^+$
- Adding more $CH_3CO_2^-$ to the solution shifts the equilibrium to the left, making the solution less acidic (higher pH).
- 0.100 M CH_3CO_2H pH = 2.879
- 0.100 M CH_3CO_2H, 0.050 M $NaCH_3CO_2$ pH = 4.456
- $CH_3CO_2^-$ is an ion common to CH_3CO_2H and $NaCH_3CO_2$ solutions, consistent with Le Chatelier's Principle

Another Example

- What is the pH of 1.00 M HF solution to which is added 0.500 M NaF? $K_a = 7.0 \times 10^{-4}$
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	HF	H_3O^+ F^-	
Initial	1.00	0	0.500
Change	-x	+x	+x
Equil.	1.00 - x	x	0.500 + x

- $x(0.500 + x)/(1.00 - x) = 7.0 \times 10^{-4}$
- Assume x << 0.500 and 1.00: $x(0.500)/1.00 = 7.0 \times 10^{-4}$
- $x = 1.40 \times 10^{-3}$, so the assumption was okay
- $pH = -\log(1.40 \times 10^{-3}) = 2.854$

Group Quiz #9

- Which of the following salts will change the pH of a solution?
  NaCl
  KNO_2
  $CrCl_3$
  LiCN
  $KClO_4$
  Na_2CO_3
  NH_4Cl
  $CaBr_2$

16.3 Buffer Solutions

- Solution of a weak acid and its conjugate base in approximately equal concentrations
- Used to control pH
- Addition of a strong acid or base shifts the pH only slightly
- $HF(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + F^-(aq)$
- Add HCl, equilibrium shifts to left to consume some of added H_3O^+

Example Problem

- What is the pH of 1.00 M HF solution? $K_a = 7.0 \times 10^{-4}$
-

	HF	H_3O^+ F^-	
Initial	1.00	0	0
Change	-x	+x	+x
Equil.	1.00 - x	x	x

- $x^2/(1.00 - x) = 7.0 \times 10^{-4}$
- Assume x << 1.00: $x^2/1.00 = 7.0 \times 10^{-4}$
- $x = 2.65 \times 10^{-2}$, so the assumption was okay
- $pH = -\log(2.65 \times 10^{-2}) = 1.576$

Buffer Solutions

- Add NaOH, some H_3O^+ is consumed to neutralize the added OH^-, and the equilibrium shifts to the right to replace some of the consumed H_3O^+
- There will be a pH change in each case, but not as much as if the HCl (or NaOH) were added to water or to HF solution (or to NaF solution)
- pH of all body fluids is controlled in this way. In blood, phosphate, carbonate, and hemoglobin all act as buffers.

Buffer Solutions

- Recall that a solution of 1.00 M HF and 0.500 M NaF has a pH of 2.854
- Now add 0.100 M HCl (assume there is no volume change)
- To find the new pH, first assume that all the added strong acid reacts to change the F^- and HF concentrations.
- [HF] = 1.00 + 0.100 = 1.100 M
- $[F^-]$ = 0.500 - 0.100 = 0.400 M

Example

- Add 0.I00 M NaOH to the 1.00 M HF/0.500 M NaF buffer. What is the new pH?
- First assume that all OH^- reacts with HF:

  [HF] = 1.00 - 0.100 = 0.900 M

  $[F^-]$ = 0.500 + 0.100 = 0.600 M
- Now solve the new acid-base system:

Buffer Solutions

- Now solve the weak acid/conjugate base system:
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	HF	H_3O^+	F^-
Initial	1.1000		0.400
Change	-x	+x	+x
Equil.	1.100 - x	x	0.400 + x

- $x(0.400 + x)/(1.100 - x) = 7.0 \times 10^{-4}$
- Assume x << 0.400 and 1.100:

  $x(0.400)/1.100 = 7.0 \times 10^{-4}$
- $x = 1.93 \times 10^{-3}$, so the assumption was okay
- $pH = -\log(1.93 \times 10^{-3}) = 2.714$

Solution

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	HF	H_3O^+	F^-
Initial	0.9000		0.600
Change	-x	+x	+x
Equil.	0.900 - x	x	0.600 + x

- $x(0.600 + x)/(0.900 - x) = 7.0 \times 10^{-4}$
- Assume x << 0.600 and 0.900:

  $x(0.600)/0.900 = 7.0 \times 10^{-4}$
- $x = 1.05 \times 10^{-3}$, so the assumption was okay
- $pH = -\log(1.05 \times 10^{-3}) = 2.979$ (started at 2.854)
- In water, pH would change from 7 to 13.

Buffer Solutions

- Water: pure ✹ 0.100 M H_3O^+, pH 7 ✹ pH 1
- Buffer: pH 2.854 ✹ pH 2.714
- If base is added, assuming no volume change, reduce the concentration of HF and increase the concentration of F^- by the corresponding amount. Then solve the weak acid/conjugate base system.

Buffer Capacity

- Buffers only work within a pH range set by the value of pK_a:

  $0.1 < [HA]/[A^-] < 10$
- Outside this range, we see little buffering effect. Review Table 15.3 for the behavior of an acetate buffer system.

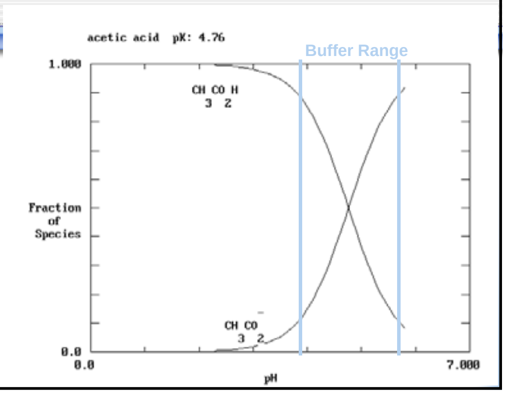
Henderson-Hasselbalch Equation

- Assuming that x << [HA] and x << [A^-] for good buffer action, the equilibrium constant expression can be rearranged to give simplified calculations:
  pH = pK_a + log([A^-]/[HA])
- Consider 1.00 M HF, 0.500 M NaF
  K_a = 7 x 10^{-4}, pK_a = 3.155
  log ([F^-]/[HF]) = log (0.500/1.00) = -0.301
  pH = 3.155 - 0.301 = 2.854 (same result as before)

Buffer Range

- We can examine the buffer range graphically by plotting the fraction as each species vs the pH
- As we move through the buffer range, one species decreases in concentration as the other increases in concentration
- See Figure 15.6
- Buffer range: pH = pK_a $\pm$ 1
- Select an appropriate acid-base pair to get within the range of the desired pH

$CH_3CO_2H/CH_3CO_2^-$



16.4 Complex Ion Equilibria

- Lewis acid-base reactions can also reach a state of equilibrium
- Metal ion + ligand ↔ complex ion
- K_f = [complex ion]/[metal ion][ligand] (formation constant)
- $Hg^{2+} + 4I^- \leftrightarrow HgI_4^{2-}$
- $K_f = [HgI_4^{2-}]/[Hg^{2+}][I^-]^4$

Complex Ion Equilibria

- Complex ions are often formed stepwise:
- $Hg^{2+} + I^- \leftrightarrow HgI^+$
  $K_{f1} = [HgI^+]/[Hg^{2+}][I^-] = 7.9 \times 10^{12}$
- $HgI^+ + I^- \leftrightarrow HgI_2$
  $K_{f2} = [HgI_2]/[HgI^+][I^-] = 1.0 \times 10^{11}$
- $HgI_2 + I^- \leftrightarrow HgI_3^-$
  $K_{f3} = [HgI_3^-]/[HgI_2][I^-] = 5.0 \times 10^3$
- $HgI_3^- + I^- \leftrightarrow HgI_4^{2-}$
  $K_{f4} = [HgI_4^{2-}]/[HgI_3^-][I^-] = 2.5 \times 10^2$

Demo: orange tornado

Complex Ion Equilibria

- Add all four equations together:
  $Hg^{2+} + 4I^- \leftrightarrow HgI_4^{2-}$
  $K_f = [HgI_4^{2-}]/[Hg^{2+}][I^-]^4$
  $K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4} = 1.0 \times 10^{30}$
- Values of K_f are listed in Table 16.4; they have a wide range of values and thus of stabilities.
- Unlike Bronsted-Lowrey polyprotic acids, successive K_f values may not differ by large factors, so there may be many species coexisting. See Figure 15.11.

15.10 Solubility and Solubility Product

- Some combinations of ions in solution form insoluble salts. Recall the solubility rules from Chapter 4; also see rules in Appendix B.
- Even insoluble salts dissolve to a small extent.
- Solubility of insoluble salts is characterized by the solubility product constant, K_{sp}.
- $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$

  $K_{sp} = [Ag^+][Cl^-] = 1.70 \times 10^{-10}$

  Use to determine conditions for precipitation

Solubility

- After setting up the equation, can solve for S:

  For $Fe(OH)_3$, $(S)(3S)^3 = 1.1 \times 10^{-36}$
  $27S^4 = 1.1 \times 10^{-36}$
  $S^4 = 4.07 \times 10^{-38}$
  $S = 4.49 \times 10^{-10}$ M
  $[Fe^{3+}] = 4.49 \times 10^{-10}$ M
  $[OH^-] = 3 \times 4.49 \times 10^{-10} = 1.35 \times 10^{-9}$
  $[Fe^{3+}][OH^-]^3 = (4.49 \times 10^{-10})(1.35 \times 10^{-9})^3$
  $= 1.1 \times 10^{-36} = K_{sp}$
- If S is known, can reverse this procedure and calculate K_{sp}.

Solubility Product Constant

- $Ag_2S(s) \leftrightarrow 2Ag^+(aq) + S^{2-}(aq)$

  $K_{sp} = [Ag^+]^2[S^{2-}] = 1.0 \times 10^{-51}$
- Some values of K_{sp} for various insoluble salts are found in Table 15.2
- We can directly compare only those salts that have the same exponents in the solubility product expression.
- If that condition is met, the lower the value of K_{sp}, the less soluble the salt.

Solubility

- $Fe(OH)_3(s) \leftrightarrow Fe^{3+}(aq) + 3OH^-(aq)$
- Can solve as well by setting up an ICE table:

Substance:	Fe^{3+}(aq)	OH^-(aq)
Initial Conc.	0.00 M	0.00 M
Change	x	3x
Equil. Conc.	x	3x

- $K_{sp} = [Fe^{3+}][OH^-]^3 = (x)(3x)^3 = 1.1 \times 10^{-36}$
- Then the solution is the same as before.

Solubility

- K_{sp} can be used to calculate the solubility, which can be compared for any salts.
- Solubility (S) = molar concentration of dissolved salt; ion concentrations are related to this by their coefficients.
- AgCl: $[Ag^+] = S$ $[Cl^-] = S$ $K_{sp} = (S)(S)$
- Ag_2S: $[Ag^+] = 2S$ $[S^{2-}] = S$ $K_{sp} = (2S)^2(S)$
- $Fe(OH)_3$: $[Fe^{3+}] = S$ $[OH^-] = 3S$ $K_{sp} = (S)(3S)^3$

16.6 Modification of Solubility with Ionic Salts

- Modify solubility to dissolve minerals and ores, to precipitate ions from solution, to separate and purify ions.
- Examples:
  - remove hardness from water by adding Na_2CO_3
  - remove Ag^+ from water by adding Cl^- to recover Ag
  - dissolve $Cu(OH)_2 \cdot CuCO_3$ to mine Cu
  - separate the rare earth ions
  - separate U^{4+} from Th^{4+}
  - separate the halide ions

Common Ion Effect

- $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$
- Common ion effect: add more Cl^- to precipitate more Ag^+ from solution.
- Saturated solution of AgCl:

  $K_{sp} = 1.70 \times 10^{-10} = [Ag^+][Cl^-] = S^2$

  $S = [Ag^+] = [Cl^-] = 1.30 \times 10^{-5}$ M
- Add 0.100 M Cl^- (>> 1.30×10^{-5}, so $[Cl^-]$= 0.100 M

  $1.70 \times 10^{-10} = [Ag^+](0.100)$

  $[Ag^+] = 1.70 \times 10^{-9}$ M

Precipitation of Ions

- Example:

  Want to separate 0.100 M Pb^{2+} from 0.100 M Ag^+, using Cl^-. How much Ag^+ is left when the Pb^{2+} begins to precipitate?

  K_{sp} of $PbCl_2 = 1.6 \times 10^{-5}$

  K_{sp} of $AgCl = 1.70 \times 10^{-10}$

Precipitation of Ions

- To precipitate an ion, we must add sufficient common ion for Q_{sp} to exceed K_{sp}.
- Example:

  How much Cl^- must be in solution to begin precipitation of Ag^+ from a 0.100 M Ag^+ solution.
- $1.70 \times 10^{-10} = (0.100)[Cl^-]$

  $[Cl^-] = 1.70 \times 10^{-10}/0.100 = 1.70 \times 10^{-9}$ M

  To dissolve $AgNO_3$ in water, with no precipitation of AgCl, we must have very pure water (no Cl^- in the water).

Precipitation of Ions

- For $PbCl_2$, $(0.100)[Cl^-]^2 = 1.6 \times 10^{-5}$

  $[Cl^-] = 0.0126$ M to begin precipitating $PbCl_2$.
- ForAgCl, $[Ag^+](0.0126) = 1.70 \times 10^{-10}$

  $[Ag^+] = 1.35 \times 10^{-8}$ M left when $PbCl_2$ begins to precipitate.
- % Ag^+ left = $100 \times 1.35 \times 10^{-8}/0.100$

  $= 1.35 \times 10^{-5}\%$

Precipitation of Ions

- Group Quiz #10: (modified from original notes!!!)

  Will a solution containing **4.0×10^{-5}** M Cl^- and **2.0×10^{-4}** M Ag^+ form a precipitate of AgCl? $K_{sp} = 1.70 \times 10^{-10}$

Insoluble Basic Salts

- Metal hydroxide solubility depends on the pH.
- $Mg(OH)_2(s) \leftrightarrow Mg^{2+}(aq) + 2OH^-(aq)$
- Adjust the pH to adjust the solubility.
- $AgCN(s) \leftrightarrow Ag^+(aq) + CN^-(aq)$

  $K_{sp} = 1.6 \times 10^{-14}$
- Add HNO_3 (why not HCl?) to dissolve:
- $CN^-(aq) + H_3O^+(aq) \leftrightarrow HCN(aq) + H_2O(l)$

  $K = 2.5 \times 10^9$

Insoluble Basic Salts

- Add the two equations (multiply the Ks):

  $AgCN(s) + H_3O^+(aq) \leftrightarrow Ag^+(aq) + HCN(aq) + H_2O(l)$

  $K = 1.6 \times 10^{-14} \times 2.5 \times 10^9 = 4.0 \times 10^{-5}$

  $= [Ag^+][HCN]/[H_3O^+]$
- Adding acid shifts the equilibrium towards products.

Solubility and Complex Ions

- Formation of complex ions can also increase solubility.
- Can dissolve AgCl with NH_3.
- $AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$
- $K_{sp} = [Ag^+][Cl^-] = 1.70 \times 10^{-10}$
- $Ag^+(aq) + 2NH_3(aq) \leftrightarrow Ag(NH_3)_2^+(aq)$
- $K_f = [Ag(NH_3)_2^+]/[Ag^+][NH_3]^2$
- Mixture of AgCl and AgBr can be separated: 5 M NH_3 dissolves AgCl, but not AgBr.