Chapter 17
Additional Aspects of Aqueous Equilibria

- Water is a common solvent. Dissolved materials can be involved in different types of chemical equilibria.

17.1 The Common Ion Effect
- Metal ions or salts containing a conjugate weak acid or base can shift the pH of a solution.
- 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. A common ion will shift a chemical equilibrium in such a direction as to get rid of some of the added ion.
- $NaCH_3CO_2$ added to a solution of CH_3CO_2H will make the solution more basic.

Common Ion Effect
- $CH_3CO_2H + H_2O \rightleftharpoons CH_3CO_2^- + H_3O^+$
- 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 LeChatelier's Principle

- 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
  $CaBr_2$

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

- What is the pH of 1.00 M HF solution to which is added 0.500 M NaF? $K_a = 7.0 \times 10^{-4}$

17.2 Buffered 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
- $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$
- Add HCl, equilibrium shifts to left to consume some of added H_3O^+

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.

Addition of acid or base to a buffer

- 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
- Now solve the weak acid/conjugate base system:
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	HF	H_3O^+	F^-
Initial	1.100	0	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 = $-\log(1.93 \times 10^{-3}) = 2.714$

- Water: pure $\rightarrow$ 0.100 M H_3O^+, pH 7 $\rightarrow$ pH 1
- Buffer: pH 2.854 $\rightarrow$ 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.

- Add 0.l00 M NaOH to the 1.00 M HF/0.500 M NaF buffer. What is the new pH?

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.

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
- $K_a = 7 \times 10^{-4}$, $pK_a = 3.155$

- 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
- Buffer range: pH = $pK_a \pm 1$
- Select an appropriate acid-base pair to get within the range of the desired pH
- $CH_3CO_2H/CH_3CO_2^-$
- HF/F^-
- NH_3/NH_4^+
- $H_3PO_4/H_2PO_4^-/HPO_4^{2-}/PO_4^{3-}$

17.3 Acid-Base Titrations

- Refer to Chapter 4 for titration calculations to determine amounts of acids or bases. Widely used for chemical analysis:
- acids in plating baths
- ascorbic acid in vitamin C tablets
- acetylsalicylic acid in aspirin tablets
- acetic acid in vinegar and wines
- NaOH in potato peeling solutions or hide dehairing solutions
- phosphoric acid in soft drinks
- Equivalence point: point in a titration where there are exactly equivalent amounts of the reactants
- End point: point in a titration where the indicator changes color; may not be exactly the same as the equivalence point
- Indicator: an acid or base which has a different color than its conjugate; characterized by a pK_a, which determines the pH range of the color change ($pK_a \pm 1$).
- $HIn + H_2O \rightleftharpoons In^- + H_3O^+$
- Color change for phenolphthalein: colorless to pink   pH = 8.2 – 10

Indicators

- The appropriate indicator for a titration depends on the strength of the acid. The indicator should be picked so its color change comes close to the equivalence point.
- Examine titration curves to see what pH changes are observed at the equivalence point

Strong Acid - Strong Base

- Note the slow change before and after the equivalence point and the rapid large change at the equivalence point.
- pH changes rapidly over the range of 3 to 11
- Which indicators would give an endpoint close to the equivalence point?
  - phenolphthalein   8.2-10

- bromcresol green   3.8-5.5
- methyl red   4.8-6.0
- litmus   5-8
- bromthymol blue   6.0-7.6
- thymol blue   1.2-2.8, 8.0-8.6

Titration Curve Calculations

- Calculate the equivalence point pH by assuming complete reaction of the acid and base, then solve any weak acid (base) equilibrium for the pH.
- Calculate the pH on either side of the equivalence point the same way, except in this case, there will be an excess of one substance.
- $[H_3O^+]_{xs} = [HCl]_{xs} = 0.002500$ mol/0.07500 L $= 0.0333$ M
- pH $= -\log(0.0333) = 1.478$
- Use this method to calculate the entire titration curve (or measure the curve with a pH meter)

Weak Acid - Strong Base

- Equivalence point pH is higher than for a strong acid - strong base titration, and the range for rapid change is narrower.
- pH $=$ pK_a at half-way point
- Must take into account the weak acid / conjugate base equilibrium.
- At the equivalence point, we have a solution of the conjugate base.
- 50.0 mL 0.100 M CH_3CO_2H + 50.0 mL 0.100 M NaOH $\rightarrow$ 100.0 mL 0.0500 M $CH_3CO_2^-$
- Calculate pH as for weak base: pH $= 8.728$
- Note narrower range of pH change (6-11); phenolphthalein okay here, but might need a different indicator for a different weak acid.

Strong Acid - Weak Base

- Equivalence point pH is lower than for a strong acid - strong base titration, and rapid change is narrowed.
- pH at equivalence point is < 7
- 0.100 M HCl + 0.100 M NH_3 gives pH $= 5.27$
- Phenolphthalein doesn't work for this titration.
- Want an indicator that changes color in the range of pH 3-7
- Methyl red is a good choice.

Weak Acid - Weak Base

- Titration curve shows major pH change in a very narrow range.
- Generally doesn't give a good titration; gets worse as K_a gets smaller.

Lewis Acid-Base (Complex Ion) Equilibria

- Lewis acid-base reactions can also reach a state of equilibrium
- Metal ion + ligand $\rightleftharpoons$ complex ion
- $K_f =$ [complex ion]/[metal ion][ligand] (formation constant)

- $Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$
- $K_f = [HgI_4^{2-}]/[Hg^{2+}][I^-]^4$
- Complex ions are often formed stepwise:
- $Hg^{2+} + I^- \rightleftharpoons HgI^+$
- $K_{f1} = [HgI^+]/[Hg^{2+}][I^-] = 7.9 \times 10^{12}$
- $HgI^+ + I^- \rightleftharpoons HgI_2$
- $K_{f2} = [HgI_2]/[HgI^+][I^-] = 1.0 \times 10^{11}$
- $HgI_2 + I^- \rightleftharpoons HgI_3^-$
- $K_{f3} = [HgI_3^-]/[HgI_2][I^-] = 5.0 \times 10^3$
- $HgI_3^- + I^- \rightleftharpoons HgI_4^{2-}$
- $K_{f4} = [HgI_4^{2-}]/[HgI_3^-][I^-] = 2.5 \times 10^2$
- Add all four equations together:
- $Hg^{2+} + 4I^- \rightleftharpoons HgI_4^{2-}$
- $K_f = [HgI_4^{2-}]/[Hg^{2+}][I^-]^4$
- $K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4} = 1.0 \times 10^{30}$
- Values of K_f are listed in Table 17.1; 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.

17.4 Solubility Equilibria
- Some combinations of ions in solution form insoluble salts. Recall the solubility rules from Chapter 4.
- Even insoluble salts dissolve to a small extent.
- Solubility of insoluble salts is characterized by the solubility product constant, K_{sp}.
- $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
- $K_{sp} = [Ag^+][Cl^-] = 1.70 \times 10^{-10}$
- Use to determine conditions for precipitation

Solubility Product Constant
- $Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq)$
- $K_{sp} = [Ag^+]^2[S^{2-}] = 1.0 \times 10^{-51}$
- 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.
- K_{sp} can be used to calculate the solubility, which can be compared for any salts.

Solubility
- 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: $[Ag^+] = 2S$ $[S^{2-}] = S$ $K_{sp} = (2S)^2(S)$

- $Fe(OH)_3$: $[Fe^{3+}] = S$ $[OH^-] = 3S$ $K_{sp} = (S)(3S)^3$
- 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}.

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

- 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.

17.5 Factors that Affect Solubility

- 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

- $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
- 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^- ($\gg 1.30 \times 10^{-5}$, so $[Cl^-] = 0.100$ M
- $1.70 \times 10^{-10} = [Ag^+](0.100)$
- $[Ag^+] = 1.70 \times 10^{-9}$ M

Insoluble Basic Salts
- Metal hydroxide solubility depends on the pH.
- $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$
- Adjust the pH to adjust the solubility.
- $AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$
- $K_{sp} = 1.6 \times 10^{-14}$
- Add HNO_3 (why not HCl?) to dissolve:
- $CN^-(aq) + H_3O^+(aq) \rightleftharpoons HCN(aq) + H_2O(l)$
- $K = 2.5 \times 10^9$
- Add the two equations (multiply the Ks):
- $AgCN(s) + H_3O^+(aq) \rightleftharpoons Ag^+(aq) + HCN(aq) + H_2O(l)$
- $K = 1.6 \times 10^{-14} \times 2.5 \times 10^9 = 4.0 \times 10^{-5}$
- $= [Ag^+][HCN]/[H_3O^+]$
- 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.
- $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
- $K_{sp} = [Ag^+][Cl^-] = 1.70 \times 10^{-10}$
- $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$
- $K_f = [Ag(NH_3)_2^+]/[Ag^+][NH_3]^2$
- Mixture of AgCl and AgBr can be separated: 5 M NH_3 dissolves AgCl, but not AgBr.

17.6 Precipitation and Separation of Ions
- To precipitate an ion, we must add sufficient common ion for Q_{sp} to exceed K_{sp}.
- Group Work:
- 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
- Will a solution containing 1.0×10^{-6} M Cl^- and 1.5×10^{-4} M Ag^+ form a precipitate of AgCl? $K_{sp} = 1.70 \times 10^{-10}$

- 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 = 1.70×10^{-10}