

Chapter 15 - Applications of Aqueous Equilibria

Neutralization Reactions

- Strong acid-strong base
 - ♦ $\text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)}$
 - ♦ What's in solution? i.e. look at the net ionic equation
- Weak acid-strong base
 - ♦ $\text{HA}_{(aq)} + \text{NaOH}_{(aq)} \rightarrow \text{NaA}_{(aq)} + \text{H}_2\text{O}_{(l)}$
 - ♦ What's in solution? i.e. net ionic equation
 - ♦ What will the pH be, roughly?
 - ♦ Example: Acetic acid and sodium hydroxide

Neutralization Reactions

- Strong acid-weak base
 - ♦ $\text{HCl}_{(aq)} + \text{NH}_3_{(aq)} \rightarrow \text{NH}_4^+_{(aq)} + \text{Cl}^-_{(aq)}$
 - ♦ What's in solution?
 - ♦ What will the pH be, roughly?
- Weak acid-weak base
 - ♦ $\text{CH}_3\text{COOH}_{(aq)} + \text{NH}_3_{(aq)} \leftrightarrow \text{NH}_4^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)}$
 - ♦ Larger K values than other combinations
 - ♦ Reaction does not proceed as far toward completion as previous 3 reactions.

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

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.

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 $\text{CH}_3\text{CO}_2\text{H}$ 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

- $\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \leftrightarrow \text{CH}_3\text{CO}_2^- + \text{H}_3\text{O}^+$
- Adding more CH_3CO_2^- to the solution shifts the equilibrium to the left, making the solution less acidic (higher pH).
- 0.100 M $\text{CH}_3\text{CO}_2\text{H}$ pH = 2.879
- 0.100 M $\text{CH}_3\text{CO}_2\text{H}$,
0.050 M NaCH_3CO_2 pH = 4.456
- CH_3CO_2^- is an ion common to $\text{CH}_3\text{CO}_2\text{H}$ and NaCH_3CO_2 solutions, consistent with Le Chatelier's Principle

Group Quiz #9

- Which of the following salts will change the pH of a solution?
NaCl
KNO₂
CrCl₃
LiCN
KClO₄
Na₂CO₃
NH₄Cl
CaBr₂

Example Problem

- What is the pH of 1.00 M HF solution? $K_a = 7.0 \times 10^{-4}$
- | | | | |
|---------|----------|-------------------------------|----------------|
| | HF | H ₃ O ⁺ | 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 $x \ll 1.00$: $x^2/1.00 = 7.0 \times 10^{-4}$
- $x = 2.65 \times 10^{-2}$, so the assumption was okay
- pH = $-\log(2.65 \times 10^{-2}) = 1.576$

Another Example

- What is the pH of 1.00 M HF solution to which is added 0.500 M NaF? $K_a = 7.0 \times 10^{-4}$
- | | | | |
|---------|----------|-------------------------------|----------------|
| | HF | H ₃ O ⁺ | 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 $x \ll 0.500$ and 1.00:
 $x(0.500)/1.00 = 7.0 \times 10^{-4}$
- $x = 1.40 \times 10^{-3}$, so the assumption was okay
- $\text{pH} = -\log(1.40 \times 10^{-3}) = 2.854$

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
- $\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$
- Add HCl, equilibrium shifts to left to consume some of added H₃O⁺

Buffer Solutions

- Add NaOH, some H₃O⁺ is consumed to neutralize the added OH⁻, and the equilibrium shifts to the right to replace some of the consumed H₃O⁺
- 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

Buffer Solutions

- Now solve the weak acid/conjugate base system:
- | | | | |
|---------|-----------|-------------------------------|----------------|
| | HF | H ₃ O ⁺ | 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 $x \ll 0.400$ 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 = $-\log(1.93 \times 10^{-3}) = 2.714$

Buffer Solutions

- Water: pure * 0.100 M H₃O⁺, 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.

Example

- Add 0.100 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:

Solution

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

Buffer Capacity

- Buffers only work within a pH range set by the value of pK_a :
$$0.1 < [\text{HA}]/[\text{A}^-] < 10$$
- 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 $x \ll [\text{HA}]$ and $x \ll [\text{A}^-]$ for good buffer action, the equilibrium constant expression can be rearranged to give simplified calculations:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

- Consider 1.00 M HF, 0.500 M NaF

$$K_a = 7 \times 10^{-4}, \text{pK}_a = 3.155$$

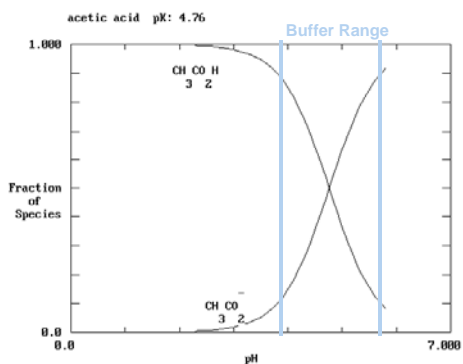
$$\log\left(\frac{[\text{F}^-]}{[\text{HF}]}\right) = \log\left(\frac{0.500}{1.00}\right) = -0.301$$

$$\text{pH} = 3.155 - 0.301 = 2.854 \text{ (same result as before)}$$

Buffer Range

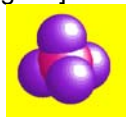
- We can examine the buffer range graphically by plotting the fraction as each species vs the pH
- As we move through the buffer range, one species decreases in concentration as the other increases in concentration
- See Figure 15.6
- Buffer range: $\text{pH} = \text{pK}_a \pm 1$
- Select an appropriate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

$\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$



16.4 Complex Ion Equilibria

- Lewis acid-base reactions can also reach a state of equilibrium
- Metal ion + ligand \leftrightarrow complex ion
- $K_f = \frac{[\text{complex ion}]}{[\text{metal ion}][\text{ligand}]}$
(formation constant)
- $\text{Hg}^{2+} + 4\text{I}^- \leftrightarrow \text{HgI}_4^{2-}$
- $K_f = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$



Complex Ion Equilibria

- Complex ions are often formed stepwise:
- $\text{Hg}^{2+} + \text{I}^- \leftrightarrow \text{HgI}^+$
 $K_{f1} = \frac{[\text{HgI}^+]}{[\text{Hg}^{2+}][\text{I}^-]} = 7.9 \times 10^{12}$
- $\text{HgI}^+ + \text{I}^- \leftrightarrow \text{HgI}_2$
 $K_{f2} = \frac{[\text{HgI}_2]}{[\text{HgI}^+][\text{I}^-]} = 1.0 \times 10^{11}$
- $\text{HgI}_2 + \text{I}^- \leftrightarrow \text{HgI}_3^-$
 $K_{f3} = \frac{[\text{HgI}_3^-]}{[\text{HgI}_2][\text{I}^-]} = 5.0 \times 10^3$
- $\text{HgI}_3^- + \text{I}^- \leftrightarrow \text{HgI}_4^{2-}$
 $K_{f4} = \frac{[\text{HgI}_4^{2-}]}{[\text{HgI}_3^-][\text{I}^-]} = 2.5 \times 10^2$

Demo: orange tornado

Complex Ion Equilibria

- Add all four equations together:
 $\text{Hg}^{2+} + 4\text{I}^- \leftrightarrow \text{HgI}_4^{2-}$
 $K_f = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$
 $K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4} = 1.0 \times 10^{30}$
- 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} .
- $\text{AgCl}(s) \leftrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$
 $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.70 \times 10^{-10}$
Use to determine conditions for precipitation



Solubility Product Constant

- $\text{Ag}_2\text{S}(s) \leftrightarrow 2\text{Ag}^+(aq) + \text{S}^{2-}(aq)$
 $K_{sp} = [\text{Ag}^+]^2[\text{S}^{2-}] = 1.0 \times 10^{-51}$
- 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

- 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 : $[\text{Ag}^+] = S$ $[\text{Cl}^-] = S$ $K_{sp} = (S)(S)$
- Ag_2S : $[\text{Ag}^+] = 2S$ $[\text{S}^{2-}] = S$ $K_{sp} = (2S)^2(S)$
- $\text{Fe}(\text{OH})_3$: $[\text{Fe}^{3+}] = S$ $[\text{OH}^-] = 3S$ $K_{sp} = (S)(3S)^3$

Solubility

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

Solubility

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

Substance:	$\text{Fe}^{3+}(\text{aq})$	$\text{OH}^-(\text{aq})$
Initial Conc.	0.00 M	0.00 M
Change	x	3x
Equil. Conc.	x	3x
- $K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = (x)(3x)^3 = 1.1 \times 10^{-36}$
- Then the solution is the same as before.

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 $\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3$ to mine Cu
 - ♦ separate the rare earth ions
 - ♦ separate U^{4+} from Th^{4+}
 - ♦ separate the halide ions



Common Ion Effect

- $\text{AgCl(s)} \leftrightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Common ion effect: add more Cl^- to precipitate more Ag^+ from solution.
- Saturated solution of AgCl :
 $K_{\text{sp}} = 1.70 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = S^2$
 $S = [\text{Ag}^+] = [\text{Cl}^-] = 1.30 \times 10^{-5} \text{ M}$
- Add 0.100 M Cl^- ($\gg 1.30 \times 10^{-5}$, so $[\text{Cl}^-] = 0.100 \text{ M}$)
 $1.70 \times 10^{-10} = [\text{Ag}^+](0.100)$
 $[\text{Ag}^+] = 1.70 \times 10^{-9} \text{ M}$

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

- **Group Quiz #10: (modified from original notes!!!)**
Will a solution containing $4.0 \times 10^{-5} \text{ M Cl}^-$ and $2.0 \times 10^{-4} \text{ M Ag}^+$ form a precipitate of AgCl ? $K_{\text{sp}} = 1.70 \times 10^{-10}$

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?

$$K_{\text{sp}} \text{ of } \text{PbCl}_2 = 1.6 \times 10^{-5}$$

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

Precipitation of Ions

- For PbCl_2 , $(0.100)[\text{Cl}^-]^2 = 1.6 \times 10^{-5}$
 $[\text{Cl}^-] = 0.0126 \text{ M}$ to begin precipitating PbCl_2 .
- For AgCl , $[\text{Ag}^+](0.0126) = 1.70 \times 10^{-10}$
 $[\text{Ag}^+] = 1.35 \times 10^{-8} \text{ M}$ left when PbCl_2 begins to precipitate.
- % Ag^+ left = $100 \times 1.35 \times 10^{-8} / 0.100$
 $= 1.35 \times 10^{-5}\%$

Insoluble Basic Salts



- Metal hydroxide solubility depends on the pH.
- $\text{Mg}(\text{OH})_2(\text{s}) \leftrightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
- Adjust the pH to adjust the solubility.
- $\text{AgCN}(\text{s}) \leftrightarrow \text{Ag}^+(\text{aq}) + \text{CN}^-(\text{aq})$
 $K_{\text{sp}} = 1.6 \times 10^{-14}$
- Add HNO_3 (why not HCl ?) to dissolve:
- $\text{CN}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \leftrightarrow \text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 $K = 2.5 \times 10^9$

Insoluble Basic Salts

- Add the two equations (multiply the Ks):
$$\text{AgCN(s)} + \text{H}_3\text{O}^+(\text{aq}) \leftrightarrow \text{Ag}^+(\text{aq}) + \text{HCN(aq)} + \text{H}_2\text{O(l)}$$
$$K = 1.6 \times 10^{-14} \times 2.5 \times 10^9 = 4.0 \times 10^{-5}$$
$$= \frac{[\text{Ag}^+][\text{HCN}]}{[\text{H}_3\text{O}^+]}$$
- 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 .
- $\text{AgCl(s)} \leftrightarrow \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.70 \times 10^{-10}$
- $\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \leftrightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq})$
- $K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$
- Mixture of AgCl and AgBr can be separated: 5 M NH_3 dissolves AgCl, but not AgBr.
