Aqueous Ionic Equilibria -- Chapter 17

1. Buffer Solutions

A *Buffer Solution* is an acid/base equilibrium system that is capable of maintaining a relatively constant pH even if a significant amount of strong acid or base is added.

(a) Components of a buffer solution:

a mixture of a weak acid and its conjugate base

e.g., acetic acid & sodium acetate (HA & A^-)

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

or, ammonium chloride & ammonia (NH_4^+ & NH_3)

$$NH_4^+{}_{(aq)} \rightleftharpoons H^+_{(aq)} + NH_{3(aq)}$$

(b) pH of buffer solution: (pH ≈ pK_a of HA)

	$HA_{(aq)}$	$\rightleftharpoons$	H^+	+	$A^-_{(aq)}$
Initial	"M"		0		"A"
Change	- x		+ x		+ x
Equil	M - x		x		A + x

$K_a = [H^+][A^-] / [HA] = x\,(A + x) / (M - x)$

since K_a is usually small ($< \sim 10^{-4}$):

$M - x \approx M$ and $A + x \approx A$

thus, $K_a \approx x\,(A) / M$ or simply,

$$\mathbf{[H^+] \approx K_a\,[HA] / [A^-]} \quad \text{(general buffer system)}$$

also, $\mathbf{[H^+] \approx K_a\,[moles\ HA / moles\ A^-]}$

(c) Buffering action (Le Châtelier's Principle)

the major equilibrium in a buffer system:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

1. What if some acid (H^+) is added?

Since H^+ is a product of above equilibrium, the reaction will shift in reverse, so that:

[HA] will increase and [A^-] will decrease

But, as long as some A^- remains, the system is still a mixture of HA and A^-. Therefore, the general equation,

$$[H^+] \approx K_a [HA] / [A^-]$$

still applies. Thus, $[H^+]$ is still $\approx K_a$

2. What if some base (OH^-) is added instead?

The added base (OH^-) will neutralize some of the acid HA and produce more of the conjugate base, A^-.

$$HA + OH^- \longrightarrow H_2O + A^-$$

[HA] will decrease and [A^-] will increase

But, as long as some HA remains, the system is still a mixture of HA and A^-, and $\therefore$ still a buffer solution.

Problems

1. (a) The pK_a of HF is 3.17. Calculate the pH of a 1.00-L solution that is 1.00 M HF and 1.50 M NaF. (b) What is the pH of this solution after addition of 50.0 mL of 10.0 M HCl?

2. What mass of solid NaCN must be added to 500 mL of 0.50 M HCN to prepare a buffer solution with a pH of 9.50?
pK_a for HCN is 9.21.

2. Acid - Base Titrations

(Review general acid-base titration concepts and terms in Chapter 4.8.)

Titration of a Weak acid by a Strong Base

e.g., 25.0 mL of 0.200 M HA (acetic acid) is titrated with 0.200 M NaOH. Determine pH in each of **four regions**:

(a) at the start -- before any NaOH is added

just a simple weak acid: pH = 2.72

(b) before the equivalence point

the acid is partially neutralized by the added OH^-

$$HA + OH^- \longrightarrow H_2O + A^-$$

since both HA and A^- are now present, the mixture is a *buffer solution* !

and $[H^+] \approx K_a$ (mole HA left) / (mole A^- produced)

e.g., after addition of 10.0 mL of NaOH, pH = 4.57

(c) at the equivalence point

the acid (HA) is completely neutralized, and

only the anion A^- is present

$\therefore$ the solution is now the *salt of a weak acid* !

total volume is now 50.0 mL, so $[A^-]$ = 0.10 M
and pH = 8.88

(d) after the equivalence point

all acid (HA) is gone and *excess* OH^- is present

$\therefore$ the pH is determined by how much OH^- is left after all the acid has been neutralized

e.g., after 40.0 mL of NaOH added: pH = 12.66

SUMMARY of Acid - Base Equilibrium Concepts (Chapters 16 and 17)

1. pH scale and the autoionization of water (K_w)
2. Strong acids and bases
3. Weak acids and bases (K_a or K_b)
4. Salts of weak acids and salts of weak bases (conjugate pairs: $K_w = K_aK_b$)
5. Buffer solutions (K_a)
   (mixture of weak acid and its conjugate base)
6. Polyprotic acids (K_{a1} and K_{a2} etc.)
7. Acid-Base Titrations
   (especially weak acid by strong base)

Do not use the Henderson-Hasselbalch Equation on the Exams ! ! !

$$pH = pK_a + \log\frac{[acid]}{[base]}$$ = No Points!

3. Solubility Equilibria

(a) "Insoluble" salts are actually sparingly soluble

equilibrium: solid salt $\rightleftharpoons$ ions in solution

e.g., In a saturated solution of Ag_2CO_3, the following equilibrium is occurring.

$$Ag_2CO_{3(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Solubility Product Constant = K_{sp}

$$K_{sp} = [Ag^+]^2\,[CO_3^{2-}] = 8.1 \times 10^{-12}$$

Given a K_{sp} value, determine the "molar solubility"

let x = molar solubility !
= moles Ag_2CO_3 dissolved / liter

$[CO_3^{2-}] = x$ and $[Ag^+] = 2x$

$$K_{sp} = 8.1 \times 10^{-12} = [Ag^+]^2\,[CO_3^{2-}] = (2x)^2\,(x)$$

$$K_{sp} = 4x^3 \qquad \therefore\ x = 1.3 \times 10^{-4}\ M$$

(b) Common ion effect:

Sparingly soluble salts are even less soluble when a "common" ion is present.

Le Châtelier's Principle applies here:

salt $\rightleftharpoons$ cation + anion

If an excess of one of the ions is present, the equilibrium will shift in reverse and less salt will dissolve!

Problem **--** Molar solubility of Ag_2CO_3 in 0.10 M Na_2CO_3 ?

let x = molar solubility of Ag_2CO_3

$[Ag^+] = 2x$ and,

$[CO_3^{2-}] = 0.10 + x$

$K_{sp} = 8.1 \times 10^{-12} = [Ag^+]^2 [CO_3^{2-}]$

$= (2x)^2 (0.10 + x)$

but since Ag_2CO_3 is not very soluble,
assume $x << 0.1$

$K_{sp} \approx (2x)^2 (0.10) \approx 8.1 \times 10^{-12}$

$\therefore x \approx 4.5 \times 10^{-6}$ M

(c) When will a precipitate form?

The solution must be saturated for a ppt to form.
Thus, the *initial* ion concentrations must be greater than the equilibrium values.

e.g., $Ag_2CO_{3(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

If *initial* concentrations of the ions are given,
calculate the **ion product**:

$Q = [Ag^+]^2 [CO_3^{2-}]$ using the *initial* conc values

If $Q > K_{sp}$ then a precipitate will form!

(d) "Insoluble" salts of weak acids are more soluble in acidic solutions

e.g., $Ag_2S_{(s)} \rightleftharpoons 2\ Ag^+_{(aq)} + S^{2-}{}_{(aq)}$

if the solution is acidic, some S^{2-} will be converted to HS^- and H_2S, thus causing more Ag_2S to dissolve

The process can be viewed as a combination of multiple equilibria, occurring simultaneously:

$$Ag_2S(s) \rightleftharpoons 2\ Ag^+(aq) + S^{2-}(aq)$$
$$H^+(aq) + S^{2-}(aq) \rightleftharpoons HS^-(aq)$$
$$H^+(aq) + HS^-(aq) \rightleftharpoons H_2S(aq)$$

Net: $Ag_2S(s) + 2\ H^+(aq) \rightleftharpoons 2\ Ag^+(aq) + H_2S(aq)$

Omit Section 17.7 -- Qualitative Analysis

4. Complex Ion Equilibria (increases solubility)

Metal ions form *complex ions* with Lewis bases, such as:

$$Cu^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$$

This type of reaction is generally very favorable so…

K is very large !

The equilibrium constant is called a Formation Constant

$$K_f = [Cu(NH_3)_4^{2+}] / [Cu^{2+}]\ [NH_3]^4$$
$$= 1.1 \times 10^{13} \quad \text{(Large !)}$$

If a complex ion can form, then an "insoluble" salt will be much more soluble (Le Châtelier Principle again !).

another example:

$$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$

Formation Constant:

$$K_f = [Ag(NH_3)_2^+] / [Ag^+]\ [NH_3]^2 = 1.6 \times 10^7$$

Problem

Given the above formation constant for $Ag(NH_3)_2^+$ and the K_{sp} value for AgBr of 5.0×10^{-13}, calculate the molar solubility of AgBr in (a) water, and (b) 0.10 M NH_3.

(a) **in water**: $AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$

$K_{sp} = [Ag^+][Br^-] = x^2 = 5.0 \times 10^{-13}$

$\therefore$ x = molar solubility $= 7.1 \times 10^{-7}$

(b) **in NH_3 solution**, two equilibria must be considered:

K_{sp}: $AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$

K_f: $Ag^+_{(aq)} + 2\ NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+_{(aq)}$

K_{net}: $AgBr_{(s)} + 2\ NH_{3(aq)} \rightleftharpoons Ag(NH_3)_2^+_{(aq)} + Br^-_{(aq)}$

$K_{net} = [Ag(NH_3)_2^+][Br^-] / [NH_3]^2$

$= K_{sp} K_f = (5.0 \times 10^{-13})(1.6 \times 10^7) = 8.0 \times 10^{-6}$

let x = molar solubility of AgBr

$[Ag(NH_3)_2^+] = [Br^-] = x$

$[NH_3] = 0.10 - 2x$ (2 : 1 stoichiometry for NH_3)

$K_{net} = x^2 / (0.10 - 2x)^2 = 8.0 \times 10^{-6}$

since K_{net} is small in this case, assume $2x << 0.10$

$x^2 / (0.10)^2 \approx 8.0 \times 10^{-6}$

$\therefore\ x \approx 2.8 \times 10^{-4}$

AgBr is about 1,000 times more soluble in NH_3 solution than in water alone.