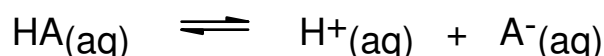# Aqueous Ionic Equilibria -- Chapter 17

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 $\approx$ 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,

[H+] $\approx K_a$ [HA] / [A⁻]   (general buffer system)

also,   **[H+] $\approx K_a$ [moles HA / moles A⁻]**

1

(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:
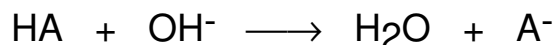
[HA] will increase and [A⁻] will decrease

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 ∴ 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.)

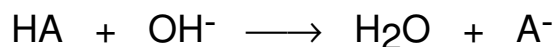### Titration of a Weak acid by a Strong Base

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

∴ 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

∴ 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: $K_W = K_a K_b$)

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
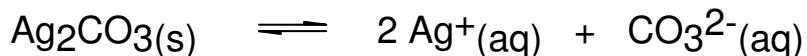Equation on the Exams ! ! !**

$$pH = pK_a + \log \frac{[acid]}{[base]}$$ = **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 $[Ag^+] = 2x$

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

$K_{sp} = 4x^3$ $\therefore$ $x = 1.3 \times 10^{-4}$ 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 x 10^{-12} = $[Ag^+]^2 [CO_3^{2-}]$

= $(2x)^2 (0.10 + x)$
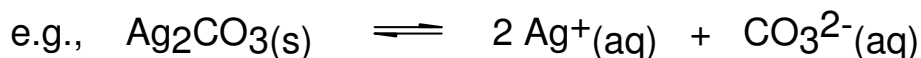
but since Ag_2CO_3 is not very soluble,
assume x << 0.1

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

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

(c) When will a precipitate form?

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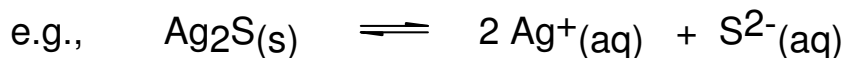Thus, the *initial* ion concentrations must be greater than the equilibrium values.

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

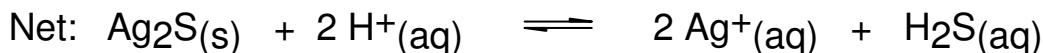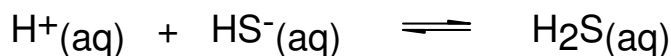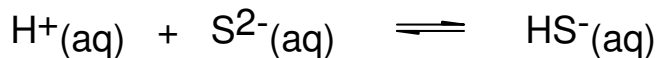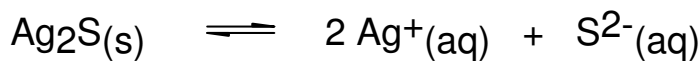### If Q > K_{sp} then a precipitate will form!

(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:

$$Cu^{2+}_{(aq)} + 4\,NH_{3(aq)} \rightleftharpoons Cu(NH_3)_4^{2+}_{(aq)}$$
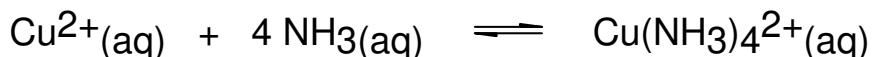
This type of reaction is generally very favorable so…

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}$ (Large !)

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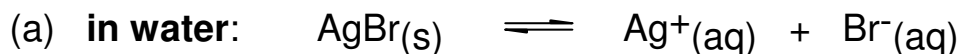
another example:

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

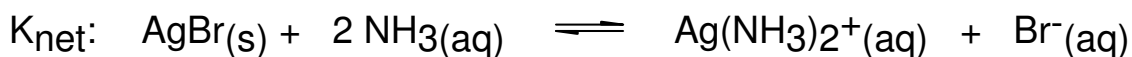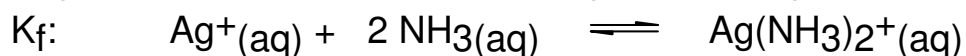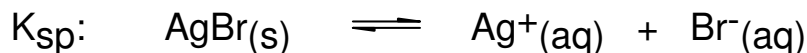Formation Constant:

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

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

$$K_{sp} = [Ag^+][Br^-] = x^2 = 5.0 \times 10^{-13}$$
$$\therefore \; x = \text{molar solubility} = 7.1 \times 10^{-7}$$

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

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

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

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

$$
\begin{aligned}
K_{net} &= [Ag(NH_3)_2^+][Br^-] / [NH_3]^2 \\
&= K_{sp}\,K_f = (5.0 \times 10^{-13})(1.6 \times 10^7) = 8.0 \times 10^{-6}
\end{aligned}
$$

let $x = $ molar solubility of AgBr

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

$[NH_3] = 0.10 - 2x \qquad$ (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 $2x \ll 0.10$

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

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

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