15 • Applications of Acid-Base Equ

STUDY GUIDE

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1. **Buffers:**

A solution that resists a change in pH when small amounts of acid or base are added.

Buffers are a mixture of
a weak acid & its conjugate base or
a weak base & its conjugate acid.

Examples:
$HC_2H_3O_2$ & $C_2H_3O_2$-
or NH_3 & NH_4^+
Your blood is a buffer.

The equilibrium is the acid equilibrium:

$$HA \rightleftharpoons H+ + A-$$

in which both the acid and its conjugate base are available to counteract the stress of adding acid or base (Le Châtelier's). The equilibrium shifts, but is almost completely counteracted by the proton donor or acceptor.

Similarly, for bases with conjugate acids:

$$B + H_2O \rightleftharpoons HB+ + OH-$$

The best buffer contains large, equal amounts of the proton donor and the proton acceptor.
$[HA] = [A^-]$ (Note: they cancel out of K_a)

Consider:

$$HA \rightleftharpoons H+ + A- \quad Ka = \frac{[H^+][A^-]}{[HA]}$$

The best buffer, $K_a = [H^+]$; $pH = pK_a$.
The pH of a buffer can be adjusted by changing the ratio of acid and base.

$$[H+] = Ka \frac{[HA]}{[A^-]}$$

$$pH = pKa - \log \frac{[HA]}{[A^-]}$$

-or- $$pH = pKa + \log \frac{[A^-]}{[HA]}$$

(Henderson-Hasselbach equation)

Similarly, for bases with conjugate acids:

$$B + H_2O \rightleftharpoons HB^+ + OH^-$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$[OH^-] = K_b \frac{[B]}{[HB^+]}$$

$$pOH = pK_b - \log \frac{[B]}{[HB^+]}$$

-or- $$pOH = pK_b + \log \frac{[HB^+]}{[B]}$$

(Henderson-Hasselbach equation)

Buffers can also be formed by changing a weak acid **into** its conjugate base by neutralizing **some** of the acid..

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

The same can be done with a weak base:

$$B + H^+ \rightarrow HB^+$$

So, a weak acid and some strong base can form a buffer. A weak base and some strong acid can also form a buffer.

2. **Titration:**

A carefully measured neutralization. Since volumes are measured, this is a "volumetric analysis."

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

A "half-titration" (neutralizing half the acid or base) forms a buffer. In that case the pH = pK_a

3. **Equivalence Point:**

The point in a titration when stoichiometric amounts of acid and base have reacted.

Note that the salt that is formed may have a pH >, <, or = 7. (Remember hydrolysis.)

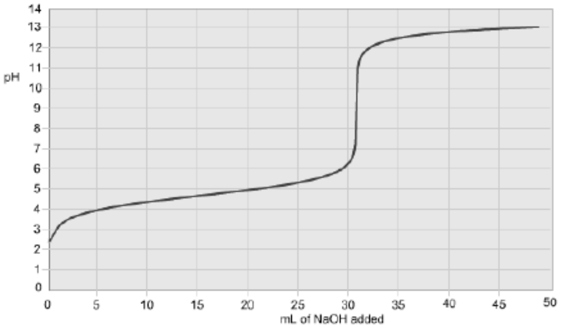
Indicators for a titration are selected based on the pH at the equivalence point.

4. **Titration Curves:**

This graph shows how the pH changes as a titration occurs.

(A) Weak acid/Strong Base

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



NOTE: Graph should have "pH" as the vertical axis and "added base" as the horizontal axis. The graph should be in an "S" shape. The middle of the lower part of the "S" indicates the point of maximum buffering where [HA]/[A-] = 1. The middle of the "S" is the equivalence point (above pH = 7) and [HA] = 0. The top part of the "S" levels off at the pH of the base solution.

(B) Weak base/Strong acid

$$B + H_3O^+ \rightleftharpoons BH^+ + H_2O$$

NOTE: Graph should have "pH" as the vertical axis and "added acid" as the horizontal axis. The graph should be in a "backwards S" shape. The middle of the upper part of the "backwards S" indicates the point of maximum buffering where [B]/[HB+] = 1. The middle of the "backwards S" is the equivalence point (below pH = 7) and [B] = 0. The bottom part of the "backwards S" levels off at the pH of the acid solution.

(C) Weak diprotic acid/Strong base

$H_2A + OH- \rightleftharpoons HA- + H_2O$

$HA- + OH- \rightleftharpoons A2- + H_2O$

NOTE: Graph should have "pH" as the vertical axis and "added base" as the horizontal axis. The graph should be in a "double S" shape. The middle of the lower part of the "first S" indicates the point of maximum buffering of the first buffering zone where $[H_2A]/[HA-] = 1$. The middle of the "first S" is the first equivalence point where $[H_2A] = 0$. The top part of the "first S" (i.e. the lower part of the "second S") indicates the point of maximum buffering of the second buffering zone where $[HA-]/[A2-] = 1$. The middle of the "second S" is the second equivalence point where $[HA-] = 0$. The top part of the "second S" levels off at the pH of the base solution.

5. **Solubility Rules**

Review/memorize these rules. They can be split into four groups:

ALWAYS SOLUBLE:

alkali metal ions (Na^+, K^+, Li^+, Rb^+, Cs^+), NH_4^+, NO_3^-, $C_2H_3O_2^-$, ClO_3^-, ClO_4^-

USUALLY SOLUBLE:

chlorides, bromides, iodides (Cl-, Br-, I-) except "AP/H" (Ag^+, Pb^{2+}, Hg_2^{2+})

sulfates (SO_4^{2-}) except "CBS/PBS" (Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+})

fluorides (F-) except "CBS/PM" (Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+})

USUALLY INSOLUBLE:

oxides/hydroxides (O^{2-}, OH^-) except "CBS" ((Ca^{2+}, Ba^{2+}, Sr^{2+})

NEVER SOLUBLE:

CO_3^{2-}, PO_4^{3-}, S^{2-}, SO_3^{2-}, CrO_4^{2-}, $C_2O_4^{2-}$ except alkali metals & NH_4^+

6. **Solubility Product (K_{sp})**

This type of equilibrium involves solids of low solubility. A saturated solution is a solution at equilibrium. The constant has no denominator.

Example: $Co(OH)_2(s) \rightleftharpoons Co^{2+} + 2OH^-$

$K_{sp} = [Co^{2+}][OH-]^2 = 2.5 \times 10^{-16}$

What is the pH of a saturated solution?

Let x = the amount (moles) of solid that will just saturate 1 L of solution.

$Co(OH)_2(s) \rightleftharpoons Co^{2+} + 2OH^-$

x	0	0
-x	+x	+2x
0	x	2x

$(x)(2x)^2 = 4x^3 = 2.5 \times 10^{-16}$

$x = 3.97 \times 10^{-6}$ $[OH-] = 2x = 7.94 \times 10^{-6}$

pOH = 5.1 pH = 14- pOH = **8.9**

7. **Solubility vs. K_{sp}**

"Molar solubility" is the concentration of the saturated solution in moles/Liter. (Solubility is sometimes reported in g/100 mL of water.)

As in the example, for a 1:2 compound, $K_{sp} = 4x^3$ (where x = solubility)

1:1	$K_{sp} = x^2$
1:2	$K_{sp} = 4x^3$
1:3	$K_{sp} = 27x^4$
2:3	$K_{sp} = 108x^5$

8. **Will a Precipitate Form?**

Ion Product (Q_{sp}) = "reaction quotient".

$Q_{sp} < K_{sp}$	more solid will dissolve
$Q_{sp} = K_{sp}$	solution is saturated
$Q_{sp} > K_{sp}$	ppt will form until $Q_{sp} = K_{sp}$

Note: Be sure to calculate concentration of DILUTED ions.

Example:

50. mL of 2.0×10^{-4} $\underline{M}$ $Co(NO_3)_2$ is mixed with 200 mL of 1.0×10^{-3} $\underline{M}$ NaOH. Will a precipitate form?

[Note:K_{sp} given in other example problem.]

$$[Co^{2+}] = 2.0 \times 10^{-4}\,\underline{M} \times \frac{50}{250} = 4.0 \times 10^{-5}\,\underline{M}$$

$$[OH-] = 1.0 \times 10^{-3}\,\underline{M} \times \frac{200}{250} = 8.0 \times 10^{-4}\,\underline{M}$$

$Q_{sp} = (4 \times 10^{-5})(8 \times 10^{-4})^2 = 2.56 \times 10^{-11}$

$Q_{sp} > K_{sp}$; a precipitate will form!

9. **Solubility can be influenced by pH.**

If the anion came from a weak acid, the salt will be more soluble in a solution of strong acid.

Example: $CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$

In a strong acid, H^+ combines with CO_3^{2-} to re-form the weak acid, H_2CO_3 (which may decompose into CO_2 & H_2O). More $CaCO_3(s)$ will dissolve to reach equilibrium.