CHAPTER 8:
ACID/BASE EQUILIBRIUM

- Already mentioned acid-base reactions in Chapter 6 when discussing reaction types.
- One way to define acids and bases is using the Brønsted-Lowry definitions.
- A Brønsted-Lowry acid donates hydrogen ions; a Brønsted-Lowry base accepts hydrogen ions.

Examples of B.L. acids and bases

$$H_3O^+_{(aq)} + OH^-_{(aq)} \leftrightarrow 2H_2O_{(l)}$$

B.L. acid B.L base both acid & base

$$CH_3COOH_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

B.L. acid B.L. base B.L. acid B.L. base

Conjugate Acids and Bases

- The reaction determines what's an acid and what's a base.

$$H_2SO_4(l) + CH_3COOH \leftrightarrow$$
$$CH_3COOH_2^+ + HSO_4^-$$

- $CH_3COOH_2^+$ is the conjugate acid of the base CH_3COOH.
- HSO_4^- is the conjugate base of H_2SO_4.
- Add H^+ to get a conjugate acid; subtract H^+ to get a conjugate base.

Strong acids and bases

- A strong acid is one which reacts almost completely with water to produce H^+. This product is the hydronium ion, H_3O^+.
  - Examples: H_2SO_4, HCl, etc.
- A strong base is one which reacts almost completely with water to produce OH^- ions.
  - Examples: KOH, $NaNH_2$

Determining pH

- The pH measures the amount of H^+ (or H_3O^+) ions.
- $pH = -\log_{10}[H_3O^+]$
- What is the pH of pure water?

$2H_2O \leftrightarrow H_3O^+(aq) + OH^-(aq)$

"Self ionization" of water

$k_w = 1.0 \times 10^{-14}$ at 25ºC = $[H_3O^+][OH^-]$

Determining the pH of water

- Pure water must be neutral, therefore $[H_3O^+] = [OH^-]$.

So,

$k_w = 10^{-14} = [H_3O^+]^2$

$[H_3O^+] = \sqrt{(10^{-14})} = 10^{-7}$ M

Therefore,

$pH = -\log_{10}(10^{-7}) = \mathbf{7}$

The pH scale

- pH < 7 is acidic

  $[H_3O^+] > [OH^-]$
- pH = 7 is neutral

  $[H_3O^+] = [OH^-]$
- pH > 7 is basic

  $[H_3O^+] < [OH^-]$

It is also possible to compute a pOH scale.

$$pOH = -\log_{10}[OH^-]$$

Strength of acids

- Stronger acids dissociate more than weaker acids (usually measured in water at 25ºC).
- A general acid, HA, would dissociate according to the equation:

$$HA\ (aq) + H_2O\ (\ell) \leftrightarrow H_3O^+ + A^-(aq)$$

$$k_a = ([H_3O^+][A^-])/[HA]*1$$

k_a and pk_a

- The bigger the constant k_a, the more the acid dissociates.
- $pk_a = -\log_{10}k_a$

Acid	k_a	pk_a
HCl	$\sim 10^7$	~ -7
H_2SO_4	$\sim 10^2$	~ -2
CH_3COOH	$\sim 1.8 \times 10^{-5}$	~ 4.74

Strength of bases

- Measures how strongly a substance wants to accept H^+.

  $H_2O(\ell) + NH_3(aq) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

  $k_b = ([NH_4^+][OH^-])/[NH_3]$

- k_b is the "basicity constant" analogous to k_a

Relationship of k_a to k_b

- Since, the autoionization reaction of water tells us that,

  $[OH^-] = (k_w/[H_3O^+])$

  then

  $k_b = ([NH_4^+][NH_3]) \times (k_w/[H_3O^+]) = k_w/k_a$

  where k_a is acidity constant of NH_4^+, the conjugate acid of NH_3.
- In general, $k_ak_b = k_w$ and

  $pk_a + pk_b = pk_w = 14$

Competition between acids and bases

- In equilibrium reactions, you can determine if reactants or products are more favored.
- For an arbitrary reactions, equilibrium constants are not usually tabulated, but can be determined from corresponding k_a and k_b values.

Competition between acids and bases (cont.)

- Consider the reaction

$HF(aq) + CN^{-}(aq) \leftrightarrow HCN(aq) + F^{-}(aq)$ **1**

- The corresponding reactions are

$HF(aq) + H_2O(\ell) \leftrightarrow H_3O^{+}(aq) + F^{-}(aq)$ **2**

$K_a = 6.6 \times 10^{-4} = ([H_3O^{+}][F^{-}])/[HF]$

$H_3O^{+}(aq) + CN^{-}(aq) \leftrightarrow HCN(aq) + H_2O(\ell)$ **3**

$(1/k_a') = (1/6.2 \times 10^{-10}) = [HCN]/([H_3O^{+}][CN^{-}])$

Competition between acids and bases (cont.)

- Reaction **1** is the sum of reactions **2** and **3**.
- When you add reactions, you multiply equilibrium constants.
- $k_{rx} = k_a * (1/k_a') = (k_a/k_a') = 1.1 \times 10^6$
- This means products are favored because HF is a stronger acid (or because CN^- is a stronger base).

Indicators

- Indicators are molecules which change colors when pH changes over a certain range.
- Phenolphthalein turns from colorless to pink as pH gets up to ~7 and higher
- Other indicators change color at different pH's.
- Indicators are not ultra-precise because the color change occurs in a pH window.

k_a's of Indicators

- An indicator in water could be represented by the reaction

  $HIn(aq) + H_2O \leftrightarrow H_3O^+(aq) + In^-(aq)$

  which has a k_a of

  $k_a = [H_3O^+][In^-]/[HIn]$
- The color starts to change as $([In^-]/[HIn]) = (k_a/[H_3O^+])$ approaches 1, that is when there are almost equal amounts of In^- and HIn (each of which has a different color).
- Color change happens when $k_a \approx [H_3O^+]$, or when $pH \approx pk_a$ of the indicator.

Equilibrium of acids and bases example

- Propionic acid CH_3CH_2COOH has a k_a = 1.3×10^{-5} at 25ºC. What is the pH of a 0.65 M solution? What fraction of the acid ionizes?

Example continued

	$[CH_3CH_2COOH]$	$[CH_3CH_2COO^-]$	$[H_3O^+]$
Start	0.65 M	~0	~0
Final			
k_a			

Example Continued

Example 2

- 0.100 mol $NaCH_3COO$ is dissolved in water to make 1.00 L of solution. What is the solution's pH?

Example 2 (cont.)

	$[CH_3COO^-]$	$[CH_3COOH]$	$[OH^-]$
Initial	0.100	0	0
Final			

Example 2

Hydrolysis

- The previous example demonstrated hydrolysis – when aqueous ions change the pH of a solution (the $NaCH_3COO$ increased the pH).
- Not all ions do this; notice that the CH_3COO^- ions grabbed protons (releasing OH^- which raised the pH) while Na^+ did not grab OH^- anions (which would have lowered the pH).

Ions and Hydrolysis

- Anions usually raise the pH by hydrolysis (exceptions: Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ClO_3^-, ClO_4^-)
- Cations usually lower the pH by hydrolysis (exceptions: Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+)

Buffer Solutions

- Solutions designed to keep pH constant (even if some acid or base is added) are called buffer solutions.
- These are often found in biological systems which need to keep a constant pH.
- How can you keep pH constant? Must be able to absorb/neutralize acid <u>or</u> base!
- To accomplish this, you typically use an acid and its conjugate base.

Example of a buffer solution

- A mixture of hypochlorous acid (HClO) and sodium hypochlorite (NaClO) (found in household bleach) is a buffer solution.
- If k_a(HClO) = 3.0×10^{-8} and 0.88 mol of HClO and 1.2 mol of NaClO are dissolved in 1.5 L of H_2O, what is the pH? What is the pH after 0.2 mol of HCl is added?

Example of buffer solution

- $HClO(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + ClO^-(aq)$
- What happens after you add the 0.2 mol HCl? It's a strong acid, so it completely dissociates.
- Since the HClO doesn't release very many protons, the ClO^- likes protons very much.
- Almost all the H^+ from HCl will combine with ClO^- to form weak HClO.

Example of a buffer solution

- Find the intial molarity of the HCl.

- Determine the initial and final concentrations.

	[HClO]	[H_3O^+]	[ClO^-]
Initial			
Final			

Example of a buffer solution – determining the new pH

Why did the pH change so little?

- 0.133 M HCl(aq) should have a pH of 0.88.
- The buffer solution works because ClO^- absorbed all of the H^+ ***and*** there was a lot of HClO already in solution, so relative amounts of both ClO^- and HClO remained about the same.
- $k_a = ([H_3O^+][A^-])/[HA] \quad \rightarrow \quad [H_3O^+] = k_a([HA]/[A^-])$
- So if $[HA]/[A^-]$ doesn't change much, then $[H_3O^+]$ won't either!

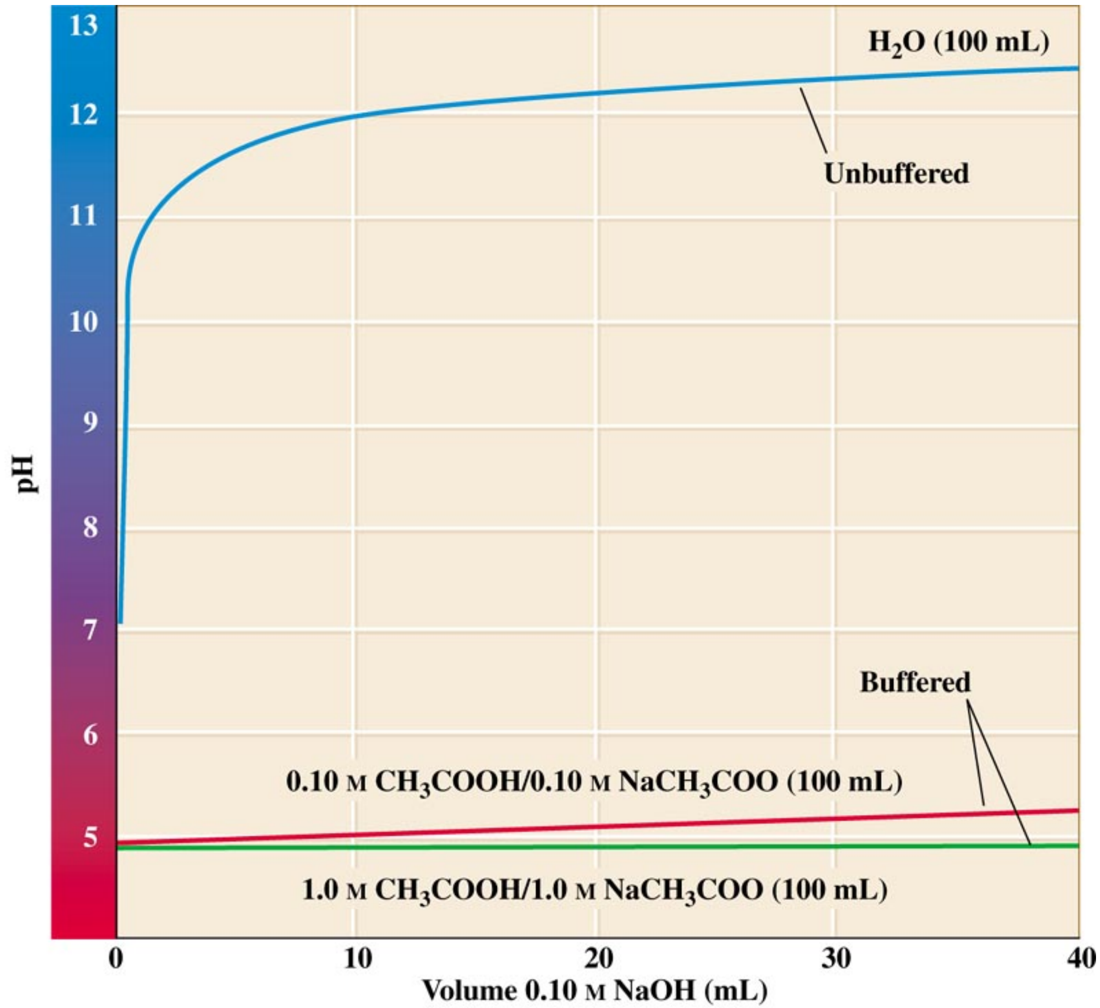
Henderson-Hassellbalch Equation

- When $[A^-] \approx [A^-]_0$ and $[HA] \approx [HA]_0$ (as in the example), $k_a = ([H_3O^+][A^-]_0)/[HA]_0$.
  which means
  $[H_3O^+] \approx ([HA]_0/[A^-]_0)k_a$
  Taking the log of everything gives:
  $pH \approx pk_a - \log_{10} ([HA]_0/[A^-]_0)$
  which is known as the
  Henderson-Hassellbalch Equation

Designing a buffer

- If you need to make a buffer for an acidic solution, use acid that's somewhat stronger (although it still must be a weak acid). You would want $k_a > 10^{-7}$.
- If you need a buffer for a basic solution, you would want $k_a < 10^{-7}$.
- If you want a buffer for a specific pH, choose a pk_a and initial concentrations to satisfy the Henderson-Hassellbalch equation. (See example 8-12).

Buffered vs. Unbuffered Solutions



Titrations and pH

- Titrations were also discussed earlier in Chapter 6, but a more detailed analysis can be done using pH.
- Generally, titrations add a basic solution to an acidic one, or vice versa. The moles of one are known accurately, the moles of the other are measured in the titration.
- At the equivalence point, $n_{acid} = n_{base}$.
- The pH change during a titration depends on whether strong acids/bases are used.

Case 1: Titration of a strong acid by a strong base

- Example: Titrating 0.1 M HCl by 0.1 M NaOH
- At the beginning, 0.1 M HCl has a pH of what?
- What's the pH when 90% of the HCl has been neutralized?

Case 1: Titration of a strong acid by a strong base

- At equivilence, 1 L of NaOH added to 1 L of HCl, neutralization, the only H_3O^+ comes from the autoionization of water.

  $2H_2O \leftrightarrow H_3O^+(aq) + OH^-(aq)$

  $[H_3O^+] = 10^{-7}$

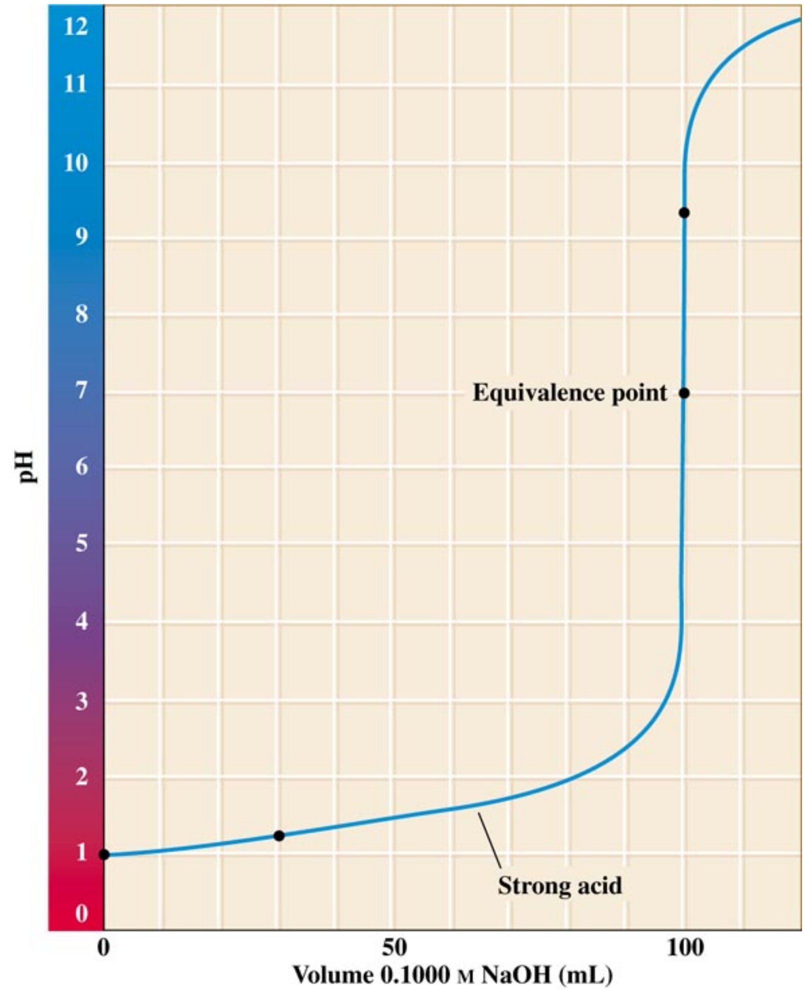
  pH = 7

Case 1: Titration of a strong acid by a strong base

- When an extra 0.1 L of NaOH is added, what's the pH?

Case 1 Summary

- pH changes slowly until equivalence, then shoots upwards rapidly, then levels off (to what value in our example?)

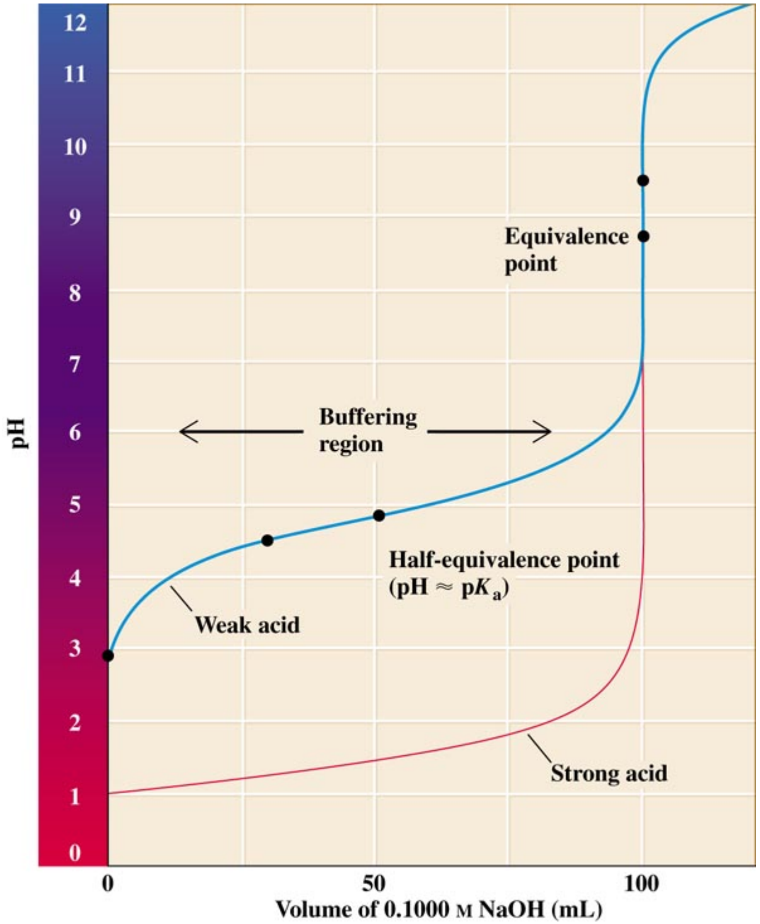


Case 2: Weak acid with strong base

- In the beginning, you have a weak acid, so pH < 7, but not very low.
- When you add a little strong base, the base reacts completely with equivalent amount of weak acid to nuetralize it, leaving a mix of weak acid and its conjugate base (note this makes a buffer solution!). The pH changes slowly.

Case 2: Weak acid with strong base

- Once more than enough strong base is added, the pH changes rapidly and then levels off.
- Notice that the equivalence point is not at pH of 7. Why? We are defining the equivalence point as where n_{acid} = n_{base}, but we have generated some of the acid's conjugate base during neutralization, and this raises the pH.



Polyprotic Acids

- Acids which can give more than one proton are called polyprotic acids.

  $H_2SO_4(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + HSO_4^-(aq)$

  $k_a \approx 100$ (huge)

  $HSO_4^-(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + SO_4^-(aq)$

  $k_{a2} = 1.2 \times 10^{-2}$ (big, but not huge)

  HSO_4^- is a weak acid

- A strong base can still take both protons from H_2SO_4 but sometimes by itself it will only give up one.

Polyprotic acid example

- Suppose we have an initial concentration of 0.034 M aqueous H_2CO_3. What are the concentrations of each species?

$H_2CO_3(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + HCO_3^-(aq)$

$k_a = 4.3 \times 10^{-7}$

$HCO_3^-(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + CO_3^{-2}(aq)$

$k_a = 4.8 \times 10^{-11}$

- Notice that $k_{a1} >> k_{a2}$, so most of the H_3O^+ comes from 1st equation, not 2nd. Likewise, most HCO_3^- comes from equation 1, relatively little used by equation 2. This suggests simplifications for setting up the problem.

Polyprotic acid example

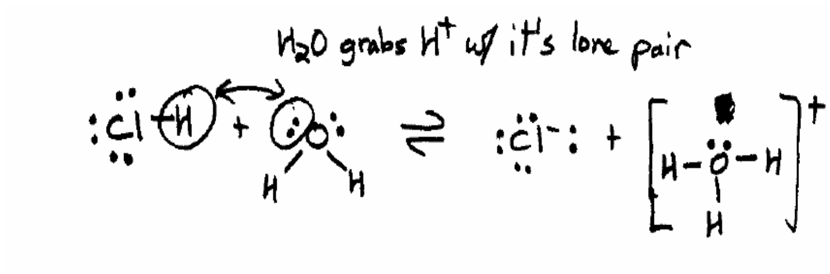
- Since $k_{a1+} >> k_{a2}$, you can solve the first equilibrium while ignoring the second (at first, anyway).

	$[H_2CO_3]$	$[H_3O^+]$	$[HCO_3^-]$
Initial			
Final			

Polyprotic example continued

Lewis acids and bases

- An alternative definition of acids and bases are the Lewis definitions
- A Lewis acid is an electron acceptor and a Lewis base is an electron donor.



Examples of Lewis acids and bases

- This allows us to say NH_3 is a Lewis base and BH_3 is a Lewis acid in a reaction.