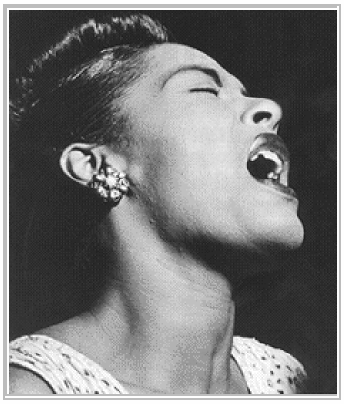
Chemistry 132 NT

Instead of having "answers" on a math test, they should just call them " impressions", and if you got a different "impression", so what, can't we all be brothers?

Jack Handey



Chem 132 NT

Acid-Base Equilibria

Module 4

Solutions of a Weak Acid or Base and Another Solute

- **The Henderson-Hasselbalch Equation**
- **Acid-Base Titration Curves**

Reaction of zinc metal with hydrochloric acid.

Review

- Calculating the common-ion effect on acid ionization.
- Calculating the pH of a buffer from given volumes of solution.

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - A buffer must be prepared from a conjugate acid-base pair in which the **K_a of the acid is approximately equal to the desired H^+ concentration**.
  - To illustrate, consider a buffer of a weak acid HA and its conjugate base A^-.

    The acid ionization equilibrium is:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - The acid ionization constant is:

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

  - By rearranging, you get an equation for the H^+ concentration.

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

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - Taking the negative logarithm of both sides of the equation we obtain:

$$-\log[H^+] = -\log(K_a) - \log\frac{[HA]}{[A^-]}$$

  - The previous equation can be rewritten

$$pH = \boxed{pK_a} + \log\boxed{\frac{[A^-]}{[HA]}}$$

inversion

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - More generally, you can write

$$pH = \boxed{pK_a} + \log\boxed{\frac{[base]}{[acid]}}$$

"fine tune"

  - This equation relates the pH of a buffer to the concentrations of the conjugate acid and base. It is known as the **Henderson-Hasselbalch equation.**

A Problem To Consider

- A buffer is prepared by adding 45.0 mL of 0.15 M NaF to 35.0 mL of 0.10 M HF. **What is the pH** of this buffer? (The K_a for HF is 6.8×10^{-4})
  - The Henderson-Hasselbalch equation is ideal for solving buffer pH problems.

The negative log of the K_a, which was given.

The concentration of F^- (from NaF).

$$pH = pK_a + \log\frac{[base]}{[acid]}$$

The concentration of HF.

A Problem To Consider

- A buffer is prepared by adding 45.0 mL of 0.15 M NaF to 35.0 mL of 0.10 M HF. **What is the pH** of this buffer? (The K_a for HF is 6.8 x 10^{-4})
  - First, let's calculate the "new" molarities of HF and F^-, once the solutions are mixed together.

$$\text{mol HF} = (0.035\,\text{L}) \times (0.10\,\tfrac{\text{mol HF}}{\text{L}}) = 0.0035\,\text{mol HF}$$

$$\text{"new" M HF} = \frac{0.0035\ \text{mol HF}}{0.080\ \text{L total volume}} = \boxed{0.044\ \text{M HF}}$$

Total volume = 0.035 L + 0.045 L = 0.080 L

A Problem To Consider

- A buffer is prepared by adding 45.0 mL of 0.15 M NaF to 35.0 mL of 0.10 M HF. **What is the pH** of this buffer? (The K_a for HF is 6.8 x 10^{-4})
  - First, let's calculate the "new" molarities of HF and F^-, once the solutions are mixed together.

$$\text{mol}\,F^- = (0.045\,\text{L}) \times (0.15\,\tfrac{\text{mol HF}}{\text{L}}) = 0.0068\,\text{mol}\,F^-$$

$$\text{"new" M}\,F^- = \frac{0.0068\,\text{mol}\,F^-}{0.080\,\text{L total volume}} = \boxed{0.084\,\text{M}\,F^-}$$

A Problem To Consider

- A buffer is prepared by adding 45.0 mL of 0.15 M NaF to 35.0 mL of 0.10 M HF. **What is the pH** of this buffer? (The K_a for HF is 6.8 x 10^{-4})
  - Now, we need the "pK_a".

$$pK_a = -\log(6.8 \times 10^{-4}) = 3.17$$

  - Now, we're ready to assemble the Henderson-Hasselbalch equation.

A Problem To Consider

- A buffer is prepared by adding 45.0 mL of 0.15 M NaF to 35.0 mL of 0.10 M HF. **What is the pH** of this buffer? (The K_a for HF is 6.8×10^{-4})
  - Substituting into the equation we get:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$pH = \boxed{(3.17)} + \log\frac{(0.084\ M\ F^-)}{(0.044\ M\ HF)}$$

$$pH = (3.17) + 0.28 = \boxed{3.45}$$

Note that the pH of a buffer will always be close to its pK_a. The log term simply "fine tunes" the buffer.

The Henderson-Hasselbalch Equation

- How do you prepare a buffer of given pH?
  - So to prepare a buffer of a given pH (for example, **pH 4.90**) we need a conjugate acid-base pair with a pK_a close to the desired pH.
  - The K_a for acetic acid is 1.7×10^{-5}, and its pK_a is 4.77.
  - You could get a buffer of pH 4.90 by increasing the ratio of [base]/[acid].

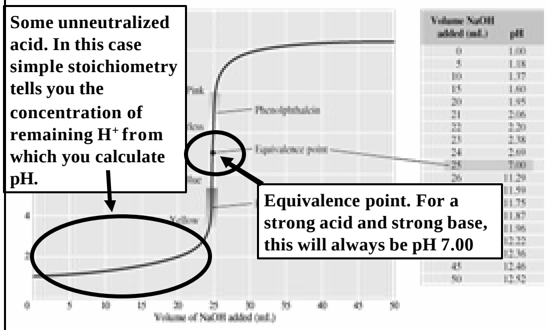
Acid-Ionization Titration Curves

- An **acid-base titration curve** is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid).
  - Such curves are used to gain insight into the titration process.
  - You can use titration curves to choose an **appropriate indicator** that will show when the titration is complete.

Titration of a Strong Acid by a Strong Base

- The figure on the next slide shows a curve for the titration of HCl with NaOH.
  - Note that the pH changes slowly until the titration approaches the equivalence point.
  - The **equivalence point** is the point in a titration when a stoichiometric amount of reactant has been added.

Curve for the titration of a strong acid by a strong base.



Some unneutralized acid. In this case simple stoichiometry tells you the concentration of remaining H^+ from which you calculate pH.

Equivalence point. For a strong acid and strong base, this will always be pH 7.00

Titration of a Strong Acid by a Strong Base

- The figure on the next slide shows a curve for the titration of HCl with NaOH.
  - At the equivalence point, the pH of the solution is 7.0 because it contains **a salt, NaCl, that does not hydrolyze**.
  - However, the pH changes rapidly from a pH of about 3 to a pH of about 11.

Titration of a Strong Acid by a Strong Base

- The figure on the next slide shows a curve for the titration of HCl with NaOH.
  - To detect the equivalence point, you need an **acid-base indicator** that changes color within the pH range 3-11.
  - Phenolphthalein can be used because it changes color in the pH range 8.2-10.

A Problem To Consider

- Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.
  - Because the reactants are a strong acid and a strong base, the reaction is essentially complete.

$$H^{+}(aq) + OH^{-}(aq) \text{ ® } H_2O(l)$$

A Problem To Consider

- Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.
  - We get the amounts of reactants by multiplying the volume of each (in liters) by their respective molarities.

$$\text{Mol } H^{+} = 0.0250\text{L} \text{ ´ } 0.100\,{}^{\text{mol}}\!/_{\text{L}} = 0.00250 \text{ mol}$$

$$\text{Mol } OH^{-} = 0.0100\text{L} \text{ ´ } 0.100\,{}^{\text{mol}}\!/_{\text{L}} = 0.00100 \text{ mol}$$

A Problem To Consider

- Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.
  - All of the OH^- reacts, leaving an excess of H^+

$$\text{Excess } H^+ = (0.00250 - 0.00100) \text{ mol}$$

$$= 0.00150 \text{ mol } H^+$$

A Problem To Consider

- Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.
  - You obtain the H^+ concentration by dividing the mol H^+ by the total volume of solution (0.0250 L + 0.0100 L=0.0350 L)

$$[H^+] = \frac{0.00150 \text{ mol}}{0.0350 \text{ L}} = 0.0429 \text{ M}$$

A Problem To Consider

- Calculate the pH of a solution in which 10.0 mL of 0.100 M NaOH is added to 25.0 mL of 0.100 M HCl.
  - Hence,

$$\text{pH} = -\log(0.0429) = 1.368$$

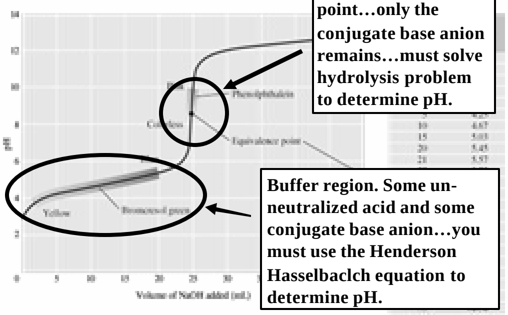
Titration of a Weak Acid by a Strong Base

- The titration of a **weak acid** by a strong base gives a somewhat different curve.
  - The pH range of these titrations is shorter.
  - Before the equivalence point is reached, we have some un-neutralized acid and it’s conjugate base anion, that is, **a buffer**.
  - The pH in this “buffer” region can be determined using the Henderson-Hasselbalch equation.

Titration of a Weak Acid by a Strong Base

- The titration of a **weak acid** by a strong base gives a somewhat different curve.
  - The **equivalence point will be on the basic side** since the salt produced contains the anion of a weak acid.
  - The figure on the next slide shows the curve for the titration of nicotinic acid with NaOH.

Curve for the titration of a weak acid by a strong base.



Equivalence point…only the conjugate base anion remains…must solve hydrolysis problem to determine pH.

Buffer region. Some un-neutralized acid and some conjugate base anion…you must use the Henderson Hasselbaclch equation to determine pH.

A Problem To Consider

- Calculate the **pH** of the solution **<u>at the equivalence point</u>** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - At the equivalence point, equal molar amounts of acetic acid and sodium hydroxide react to give sodium acetate.

A Problem To Consider

- Calculate the **pH** of the solution **<u>at the equivalence point</u>** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - First, calculate the concentration of the acetate ion.
  - In this case, 25.0 mL of 0.10 M NaOH is needed to react with 25.0 mL of 0.10 M acetic acid.

A Problem To Consider

- Calculate the **pH** of the solution **<u>at the equivalence point</u>** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - The molar amount of acetate ion formed equals the initial molar amount of acetic acid.

$$0.025\ \text{L soln} \times \frac{0.10\ \text{mol}\ C_2H_3O_2^-}{1\ \text{L soln}} = 0.0025\ \text{mol}\ C_2H_3O_2^-$$

A Problem To Consider

- Calculate the **pH** of the solution **<u>at the equivalence point</u>** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - The total volume of the solution is 50.0 mL. Hence,

$$M\ C_2H_3O_2^- = \frac{0.0025\,mol\,C_2H_3O_2^-}{0.050\,L} = 0.050\,M$$

A Problem To Consider

- Calculate the **pH** of the solution **<u>at the equivalence point</u>** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - The hydrolysis of this 0.05 M acetate ion solution follows the mechanism given in an earlier module of this chapter.

$$C_2H_3O_2^- + H_2O \leftrightharpoons HC_2H_3O_2 + OH^-$$

$$K_b(\text{for } C_2H_3O_2^-) = \frac{K_w}{K_a(\text{for } HC_2H_3O_2)}$$

A Problem To Consider

- Calculate the **pH** of the solution **<u>at the equivalence point</u>** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7×10^{-5}.
  - The hydrolysis of this 0.05 M acetate ion solution follows the mechanism given in an earlier module of this chapter.

$$C_2H_3O_2^- + H_2O \leftrightharpoons HC_2H_3O_2 + OH^-$$

(0.05 – “x”) **(“x”)** **(“x”)**

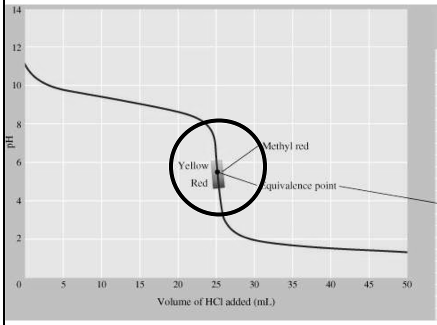
A Problem To Consider

- Calculate the **pH** of the solution **at the equivalence point** when 25.0 mL of 0.10 M acetic acid is titrated with 0.10 M sodium hydroxide. The K_a for acetic acid is 1.7 x 10^{-5}.
  - The hydrolysis of this 0.05 M acetate ion solution follows the mechanism given in an earlier module of this chapter.
  - You find the K_b for the acetate ion to be 5.9 x 10^{-10} and that the concentration of the hydroxide ion is 5.4 x 10^{-6}. **The pH is 8.73**

Titration of a Weak Base by a Strong Acid

- The titration of a **weak base** with a **strong acid** is a reflection of our previous example.
  - The figure on the next slide shows the titration of NH_3 with HCl.
  - In this case, the pH declines slowly at first, then falls abruptly from about pH 7 to pH 3.
  - Methyl red, which changes color from yellow at pH 6 to red at pH 4.8, is a possible indicator.

Curve for the titration of a weak base by a strong acid.



Volume HCl added (mL)	pH
0	11.13
1	10.64
2	10.32
3	10.13
4	9.98
5	9.86
10	9.44
15	9.08
20	8.66
21	8.54
22	8.39
23	8.20
24	7.88
25	5.28
26	2.70
27	2.40
28	2.22
29	2.10
30	2.00
35	1.70
40	1.52
45	1.40
50	1.30

A Little "Trick"

- At the "half-way" point in the titration of a weak acid with a strong base, we can make a significant simplification.
  - **At the halfway point** in such a titration, exactly half of the original acid has been converted to its conjugate base anion.

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

This means that $[A^-] = [HA]$

A Little "Trick"

- At the "half-way" point in the titration of a weak acid with a strong base, we can make a significant simplification.
  - **At the halfway point** in such a titration, exactly half of the original acid has been converted to its conjugate base anion.

$$\mathrm{pH} = \mathrm{pK_a} + \log(1)$$

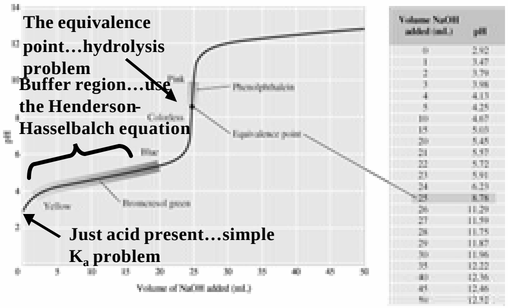
$$\mathrm{pH} = \mathrm{pK_a}$$

The pH = pK_a only at the halfway point. We'll use this fact in lab to determine the K_a of an unknown acid.

Operational Skills

- Using the Henderson-Hasselbalch equation.
- Calculating the pH of a solution of a strong acid and a strong base
- Calculating the pH at the equivalence point in the titration of a weak acid with a strong base

Summary



Volume NaOH added (mL)	pH
0	2.92
1	3.47
2	3.79
3	3.98
4	4.13
5	4.25
10	4.67
15	5.03
20	5.45
21	5.57
22	5.72
23	5.91
24	6.23
25	8.78
26	11.29
27	11.59
28	11.75
29	11.87
30	11.96
35	12.22
40	12.36
45	12.46
50	12.52

The equivalence point…hydrolysis problem

Buffer region…use the Henderson-Hasselbalch equation

Just acid present…simple K_a problem

Operational Skills

Time for a few review questions