**ACID-BASE REACTIONS**

Chapter 14
("Part II")

A Weak Acid + Strong Base

Titration

### Titrations

In this technique a known concentration of base (or acid) is slowly added to a solution of acid (or base). A pH meter or indicators are used to determine when the solution has reached the equivalence point where moles of acid = moles of base.

Adding NaOH from the buret to acetic acid:

Initially the pH increases very slowly, then rises dramatically at equivalence point. pH rises, then levels off as equivalence point passed.

Notice how [HOAc] diminishes with NaOH, but [OAc\^-] increases with NaOH.

Important to consider conjugates in titrations where weak acids or bases dominate. But first, buffers and the common ion effect.

### The Common Ion Effect

A special form of Le Chatelier’s Principle...

**QUESTION:** What is the effect on the pH of adding NH\_4Cl to 0.25 M NH\_3(aq)?

\[
\text{NH}_3(aq) + H_2O \rightleftharpoons \text{NH}_4^+(aq) + OH^-(aq)
\]

Here we are adding an ion COMMON to the equilibrium with NH\_3 (i.e. NH\_4\^+).

Le Chatelier predicts that the equilibrium will shift to the ____________.

The pH will go ____________.

After all, NH\_4\^+ is an acid!

### The Common Ion Effect

A special form of Le Chatelier’s Principle...

**QUESTION:** What is the effect on the pH of adding NH\_4Cl to 0.25 M NH\_3(aq)?

\[
\text{NH}_3(aq) + H_2O \rightleftharpoons \text{NH}_4^+(aq) + OH^-(aq)
\]

Let us first calculate the pH of a 0.25 M NH\_3 solution.

\[
\begin{align*}
\text{initial} &\quad \text{change} \\
[\text{NH}_3] &\quad \text{[NH}_4^+] \quad \text{[OH]} \\
[\text{NH}_3] &\quad \text{[NH}_4^+] \quad \text{[OH]} \\
\end{align*}
\]

**initial change equilib**
The Common Ion Effect

A special form of Le Chatelier's Principle...

**QUESTION:** What is the effect on the pH of adding NH₄Cl to 0.25 M NH₃(aq)?

NH₃(aq) + H₂O ⇌ NH₄⁺(aq) + OH⁻(aq)

\[ K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} \]

Assuming \( x \) is << 0.25, we have

\[ [OH^-] = x = \sqrt{K_b \times c} = 0.0021 \text{ M} \]

This gives pOH = 2.67

and so pH = 14.00 - 2.67 = 11.33

or: \( \text{pH} = 14 + \log([K_b \cdot C_b])^{1/2} = 11.33 \)

A special form of Le Chatelier's Principle...

**Problem:** What is the pH of a solution with 0.10 M NH₄Cl and 0.25 M NH₃(aq)?

NH₃(aq) + H₂O ⇌ NH₄⁺(aq) + OH⁻(aq)

We expect that the pH will decline on adding NH₄Cl. Let's test that!

\[ [NH_3] [NH_4^+] [OH^-] \]

initial change equilib

Because equilibrium shifts left, \( x \) is MUCH less than 0.0021 M, the value **without** NH₄Cl.

Buffer Solutions

The function of a buffer is to resist changes in the pH of a solution.

Buffers invoke a special case of the common ion effect.

**Buffer Composition:**

- Weak Acid + Conj. Base
- HOAc + OAc⁻
- H₂PO₄⁻ + HPO₄²⁻
- Weak Base + Conj. Acid
- NH₃ + NH₄⁺

Buffers and Henderson-Hasselbalch Guide

The blood pH in our bodies is regulated by a carbonic acid / hydrogen carbonate ("bicarbonate") buffer system:

CO₂ + H₂O ⇌ H₂CO₃ ⇌ H⁺ + HCO₃⁻

CO₂ + NaHCO₃ ⇌ H₂CO₃ + Na⁺

Exhaling CO₂ raises the pH of our blood!
Buffer Solutions

** Buffer Solutions **

** Consider HOAc/OAc⁻ to see how buffers work **

** Conjugate base in buffers consumes strong acid! **

\[
\ce{HOAc + H2O ⇌ OAc⁻ + H3O⁺} \\
K_a = 1.8 \times 10^{-5}
\]

Therefore, the reverse reaction of the weak base with added \( \text{H}_2\text{O}^+ \) (strong acid) would be:

\[
\ce{OAc⁻ + H2O⁺ ⇌ HOAc + H2O} \\
K_{\text{reverse}} = 1/K_a = 5.6 \times 10^4
\]

\( K_{\text{reverse}} \) is VERY LARGE, so OAc⁻ completely consumes the \( \text{H}_2\text{O}^+ \)!

---

** Problem: ** What is the pH of a buffer that has \([\text{HOAc}] = 0.700 \ \text{M} \) and \([\text{OAc}⁻] = 0.600 \ \text{M}\)?

\[
\begin{align*}
\text{HOAc} + \text{H}_2\text{O} &\rightleftharpoons \text{OAc}⁻ + \text{H}_3\text{O}⁺ \\
K_a &= 1.8 \times 10^{-5}
\end{align*}
\]

\[
\begin{align*}
\text{initial} & & \text{change} & & \text{equilib} \\
[\text{HOAc}] & & [\text{OAc}⁻] & & [\text{H}_3\text{O}⁺] \\
0.700 & & 0.600 & & x
\end{align*}
\]

\[
\begin{align*}
K_a &= 1.8 \times 10^{-5} \\
= & \frac{[\text{H}_3\text{O}⁺][\text{OAc}⁻]}{[\text{HOAc}]}
\end{align*}
\]

Assuming that \( x \ll 0.700 \) and 0.600, we have

\[
\begin{align*}
K_a &= 1.8 \times 10^{-5} \\
&= \frac{[\text{H}_3\text{O}⁺][0.600]}{0.700}
\end{align*}
\]

\[
[\text{H}_3\text{O}⁺] = 1.8 \times 10^{-5} \cdot (0.700 / 0.600) = 2.1 \times 10^{-5} \ and \ pH = 4.68
\]
Buffer Solutions

Notice that the expression for calculating the H⁺ conc. of the buffer is:

\[
[H_3O^+] = \frac{\text{Orig. conc. of HOAc}}{\text{Orig. conc. of OAc}^-} \cdot K_a
\]

\[
[H_3O^+] = \frac{[\text{Acid}]}{[\text{Conj. base}]} \cdot K_a \quad \text{or} \quad [\text{OH}^-] = \frac{[\text{Base}]}{[\text{Conj. acid}]} \cdot K_b
\]

Notice that [H₃O⁺] or [OH⁻] depend on K and the ratio of acid and base concentrations.

Henderson-Hasselbalch Equation

\[
pH = pK_a - \log \left( \frac{[\text{Acid}]}{[\text{Conj. base}]} \right)
\]

The pH is determined largely by the pKₐ of the acid and then adjusted by the ratio of acid and conjugate base. Important equation!

Adding an Acid to a Buffer

Problem: What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (before HCl, pH = 7.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc⁻] = 0.600 M (pH = 4.68)

Solution to Part (a)

\[
\text{pH of strong acid} = - \log [H_3O^+] = - \log [\text{HCl}]
\]

\[
M_1 \cdot V_1 = M_2 \cdot V_2
\]

\[
1.00 \text{ M} \cdot 1.00 \text{ mL} = M_2 \cdot 1001 \text{ mL}
\]

\[
M_2 = 9.99 \times 10^{-4} \text{ M} = [H_3O^+] = [OH^-]
\]

\[
pH = 3.00
\]

Solution to Part (b)

Step 1 - do the stoichiometry

\[
\text{H}_3\text{O}^+ \text{ (from HCl)} + \text{OAc}^- \text{ (from buffer)} \rightarrow \text{HOAc} \text{ (from buffer)}
\]

The reaction occurs completely because K is very large.

Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (after HCl, pH = 3.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc⁻] = 0.600 M (pH = 4.68)

Solution to Part (b):

Initial

\[
\begin{align*}
[H_3O^+] & \quad [\text{OAc}^-] & \quad [\text{HOAc}]
\end{align*}
\]

Change

After rxn

Now we need to calculate pH using our new buffer solution.
Adding an Acid to a Buffer

What is the pH when 1.00 mL of 1.00 M HCl is added to:

a) 1.00 L of pure water (after HCl, pH = 3.00)
b) 1.00 L of buffer that has [HOAc] = 0.700 M and [OAc\(^-\)] = 0.600 M (pH = 4.68)

Solution to Part (b): Step 2 - Equilibrium

\[
\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^-
\]

Initial

\[
\begin{array}{c|c|c|c}
\text{[HOAc]} & \text{[OAc\(^-\)]} & \text{[H}_3\text{O}^+\] \\
\hline
\text{0.701} & \text{0.599} & \text{0}
\end{array}
\]

Change

\[
\begin{array}{c|c|c|c}
\hline
\text{-x} & \text{+x} & \text{+x} \\
\end{array}
\]

Equilibrium

\[
\begin{array}{c|c|c|c}
\text{[HOAc]} & \text{[OAc\(^-\)]} & \text{[H}_3\text{O}^+\] \\
\hline
\text{0.701-x} & \text{0.599+x} & \text{x}
\end{array}
\]

Adding Acids and Bases to Buffers

For adding strong acids to buffers:

\[
\text{pH} = \text{pK}_a + \log \left( \frac{\text{mol\ Conj base - mol\ strong acid}}{\text{mol\ weak acid + mol\ strong acid}} \right)
\]

For adding strong bases to buffers:

\[
\text{pH} = \text{pK}_b + \log \left( \frac{\text{mol\ Conj base + mol\ strong base}}{\text{mol\ weak acid - mol\ strong base}} \right)
\]

Very useful for calculating pH changes in buffers!

Preparing a Buffer

You want to create a buffer solution with a pH = 4.30.

This means [H\(_3\)O\(^+\)] = 10\(^{-pH}\) = 5.0 x 10\(^{-5}\) M

It is best to choose an acid such that:

\* [H\(_3\)O\(^+\)] \approx K_a, or
\* pH \approx pK_a

You get the exact [H\(_3\)O\(^+\)] (or pH) by adjusting the ratio of weak acid to conjugate base.

For a pH = 4.30 buffer, we will look for a value of K_a = 5.0 x 10\(^{-5}\) or a pK_a = 4.30
Preparing a Buffer

You wish to create a buffer solution at pH = 4.30 (or \([H_3O^+] = 5.0 \times 10^{-5} \text{ M}\)). Which of these buffer combinations should you select?

<table>
<thead>
<tr>
<th>POSSIBLE BUFFERS</th>
<th>(K_a)</th>
<th>(pK_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO(_4^-) / SO(_4^{2-})</td>
<td>1.2 \times 10^{-2}</td>
<td>1.92</td>
</tr>
<tr>
<td>HOAc / OAc(^-)</td>
<td>1.8 \times 10^{-5}</td>
<td>4.74</td>
</tr>
<tr>
<td>HCN / CN(^-)</td>
<td>4.0 \times 10^{-10}</td>
<td>9.40</td>
</tr>
</tbody>
</table>

Best choice is acetic acid / acetate - closest in \([H_3O^+]\) to \(K_a\) or pH to \(pK_a\)!

---

Preparing a Buffer Solution

Buffer prepared from
- 8.4 g NaHCO\(_3\)
- weak acid
- 16.0 g Na\(_2\)CO\(_3\)
- conjugate base

HCO\(_3\^-\) + H\(_2\)O ⇌ H\(_3\)O\(^+\) + CO\(_3^{2-}\)

What is the pH?

**Check yourself! Answer: 10.50**

---

Titration Calculations

Allow us to calculate pH at any point in a titration.

We will study four types of titrations:
- SA + SB (equivalence pH = 7)
- SB + SA (equivalence pH = 7)
- WA + SB (equivalence pH > 7)
- WB + SA (equivalence pH < 7)

Titrations separated into regions each with their own pH formula.

Buffers used in WA + SB and WB + SA
We will do examples of all four as practice in lab.

**See Titration Guide.**
Acid-Base Reactions

**QUESTION:** You titrate 50. mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH after 45 mL of NaOH have been added?

**SOLUTION:**

```
First, determine which region of a strong acid and strong base titration to use by comparing mol HCl to mol NaOH

n_{HCl} = 0.050 L * 0.100 M = 0.0050 mol HCl
n_{NaOH} = 0.045 L * 0.100 M = 0.0045 mol NaOH

Since n_{HCl} > n_{NaOH}, this pH will fall in the pre-equivalence region
```

From before: n_{HCl} = 0.0050 mol, n_{NaOH} = 0.0045 mol

```
\[ pH = \log \left( \frac{n_{NaOH} - n_{HCl}}{n_{HCl} + n_{NaOH}} \right) \]
```

```
\[ pH = \log \left( \frac{0.0050 - 0.0045}{0.0050 + 0.0045} \right) \]
```

```
pH = 2.3
```
Acid-Base Reactions

QUESTION: You titrate 50 mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH at the equivalence point?

At equivalence, HCl + NaOH → Na+ + Cl− + H2O

Only species present at equivalence are Na+, Cl− and water.

Na+ and Cl− are conjugates of strong bases and acids; hence, they have no effect on the pH.

pH at equivalence point will be equal to 7 (neutral) due to presence of water.

The volume required to get to equivalence:

0.0050 mol HCl * (mol NaOH / mol HCl) * (L/0.100 mol NaOH) = 0.050 L or 50 mL.

Acid-Base Reactions

QUESTION: You titrate 50 mL of a 0.100 M solution of HCl with 0.100 M NaOH. What is the pH after 55 mL of NaOH have been added?

SOLUTION: (from before, nsa = 0.0050 mol)

It took 50 mL of NaOH to reach equivalence; hence, we are now in the post-equivalence region

nsb = 0.100 M * 0.055 L = 0.0055 mol

\[ \text{pH} = 14 + \log \left( \frac{\text{nsb} - \text{nsa}}{V_{\text{sa}} + V_{\text{sb}}} \right) \]

\[ \text{pH} = 14 + \log \left( \frac{0.0055 - 0.0050}{0.055 + 0.050} \right) \]

\[ \text{pH} = 14 + (-2.3) = 11.7 \]

Strong Base + Strong Acid

Notice similarities between SA + SB and SB + SA titrations!

A strong base + strong acid titration

\[ \text{pH = 14 + log} \left( \frac{\text{nsb} - \text{nsa}}{V_{\text{sa}} + V_{\text{sb}}} \right) \]

\[ \text{pH = 7 (neutral salt + water)} \]

\[ \text{pK_a} \]

\[ \text{At half-equivalence, pH = pK_a} \]

Weak Acid + Strong Base

Equivalence point dominated by conjugate base of weak acid

A weak acid + strong base titration

Pre-equivalence has weak acid and its conjugate base, acts like a "buffer"
Acid-Base Reactions

QUESTION: You titrate 100 mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH of the initial solution? Ka = 6.3 x 10^-5

HBz + H₂O ⇌ Bz⁻ + H₃O⁺

SOLUTION:

For weak acids,

\[
\text{pH} = -\log(K_a C_{\text{initial}})
\]

\[
\text{pH} = -\log\left(6.3 \times 10^{-5} \times 0.025\right)
\]

\[
\text{pH} = 2.90
\]
Acid-Base Reactions

QUESTION: You titrate 100 mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 12.5 mL of NaOH have been added? Ka = 6.3 x 10^{-5}

Before: \( n_{wa} = 0.0025 \) mol, \( pK_a = 4.20 \), \( n_{sb} = 0.00125 \) mol
When \( n_{sb} = \frac{1}{2} n_{wa} \), this is called the half-equivalence region
\( pH = pK_a \) at the half-equivalence point

Useful method of finding \( K_a \) (and \( K_b \)) values
Also, the volume of titrant (NaOH) at half equivalence is exactly half the volume necessary to reach equivalence
We will need (2x12.5) = 25 mL of NaOH to reach equivalence!

Acid-Base Reactions

QUESTION: You titrate 100 mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the equivalence point. What is the pH at the equivalence point? Ka = 6.3 x 10^{-5}

At equivalence, HBz + NaOH \( \rightarrow \) Na+ + Bz- + H2O

mol NaOH = mol HBz, or NaOH annihilates HBz
mol HBz = mol Bz at equivalence, and pH dominated by conjugate base of weak acid

\( pH \) at equivalence point will be basic when titrating a weak acid with a strong base!

\[
pH = 14 + \log \left( \frac{n_{sb}}{V_{sb} + V_{wa}} \right)
\]

\[
pH = 14 + \log \left( \frac{0.0026}{0.026 + 0.100} \right)
\]

\[ pH = 14 + (-3.10) = 10.9 \]

Acid-Base Reactions

QUESTION: You titrate 100 mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. What is the pH after 26.0 mL of NaOH have been added?

SOLUTION: (from before, \( n_{wa} = 0.0025 \) mol)

It took 25 mL of NaOH to reach equivalence; hence, we are now in the post-equivalence region
\( n_{sb} = 0.100 \) M * 0.026 L = 0.0026 mol

\[
pH = 14 + \log \left( \frac{n_{sb} - n_{wa}}{V_{sb} + V_{wa}} \right)
\]

\[
pH = 14 + \log \left( \frac{0.0026 - 0.0025}{0.026 + 0.100} \right)
\]

\[ pH = 14 + (-3.10) = 10.9 \]

Acid-Base Reactions

Benzoic acid + NaOH Titration Graph

\[ pH \text{ at } 26.0 \text{ mL} = 10.9 \]

\[ pH \text{ at half-equiv (12.5 mL)} = 4.20 \]

\[ pH \text{ at 25 mL} = 8.25 \]

\[ pH \text{ at 10 mL} = 4.02 \]

\[ pH \text{ at equivalence (25 mL)} = 8.25 \]

With weaker acids, the initial pH is higher and pH changes near the equivalence point are more subtle.
Polyprotic Acids

Titrations of polyprotic acids with bases have multiple equivalence points (and half equivalence points) for each dissociation.

Weak Base + Strong Acid

Equivalence point dominated by conjugate acid of weak base

A weak base + strong acid titration

Pre-equivalence has weak base and its conjugate acid, acts like a "buffer"

At half-equivalence, pH = pK_a

Initial:

Pre-equivalence:

Equivalence:

Post-equivalence:

Weak Base + Strong Acid

Initial:

Pre-equivalence:

Equivalence:

Post-equivalence:

Weak Base + Strong Acid

Initial:

Pre-equivalence:

Equivalence:

Post-equivalence:

pH Indicators

Equivalence point important in titration, can use an indicator to signify equivalence point

Indicator color change must reflect equivalence point to be useful!

Focus on bromthymol blue for next slide

Color Changes for Bromthymol Blue

pH Indicators

Which indicator to use?

Phenolphthalein or Methyl Red?

The pH at the equivalence point in this titration is < 7.

Methyl red is the indicator of choice here.
End of Chapter 14
Part II

See:
• Chapter Fourteen Part II Study Guide
• Chapter Fourteen Part II Concept Guide
• Types of Equilibrium Constants
• Titration Guide
• Buffers and Henderson-Hasselbalch Guide
• Important Equations (following this slide)
• End of Chapter Problems (following this slide)

End of Chapter Problems: Test Yourself

See practice problem set #3 for additional titration and buffer examples.

1. Does the pH of the solution increase, decrease, or stay the same when you:
a) Add solid ammonium chloride to a dilute aqueous solution of NH₃; b) Add solid sodium acetate to a dilute aqueous solution of acetic acid; c) Add solid NaCl to a dilute aqueous solution of NaOH?
2. For each of the following cases, decide whether the pH is less than 7, equal to 7, or greater than 7: a) equal volumes of 0.10 M acetic acid, CH₃CO₂H, and 0.10 M KOH are mixed; b) 25 mL of 0.015 M NH₃ is mixed with 25 mL of 0.015 M HCl; c) 150 mL of 0.20 M HNO₃ is mixed with 75 mL of 0.40 M NaOH
3. What is the pH of a solution that consists of 0.20 M ammonia, NH₃, and 0.20 M ammonium chloride, NH₄Cl? (Kₐ = 5.6 x 10⁻¹⁰)
4. What mass of sodium acetate, NaCH₃CO₂, must be added to 1.00 L of 0.10 M acetic acid to give a solution with a pH of 4.50? (Kₐ = 1.8 x 10⁻⁵)
5. Phenol, C₆H₅OH, is a weak organic acid. Suppose 0.515 g of the compound is dissolved in exactly 125 mL of water. The resulting solution is titrated with 0.123 M NaOH: C₆H₅OH(aq) + OH⁻(aq) → C₆H₅O⁻(aq) + H₂O(l)
   a) What is the pH of the original solution of phenol? b) What are the concentrations of all of the following ions at the equivalence point: Na⁺, H₂O⁺, OH⁻, and C₆H₅O⁻? c) What is the pH of the solution at the equivalence point?

End of Chapter Problems: Answers

1. a) pH decreases; b) pH increases; c) no change to pH
2. a. pH > 7  b. pH < 7  c. pH = 7
3. pH = 9.25
4. 4.7 g
5. a) pH = 5.62  b) [Na⁺] = 3.23 x 10⁻² mol/L, [H₂O⁺] = 6.5 x 10⁻¹² mol/L, [OH⁻] = 1.5 x 10⁻³ mol/L, and [C₆H₅O⁻] = 3.07 x 10⁻² mol/L  c) pH = 11.19

See practice problem set #3 for additional titration and buffer examples.