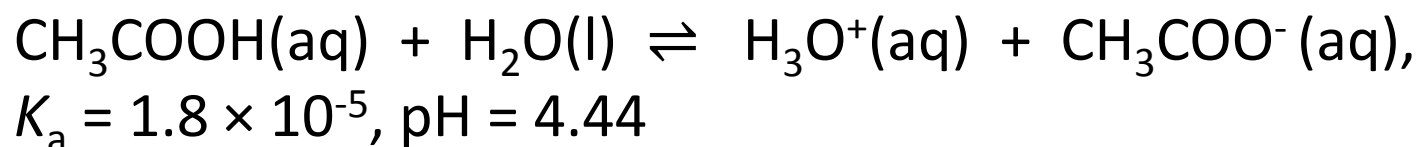


Recap

- ☐ pH of weak acid/base
- ☐ pH of salt (conjugate weak acid/base)
- ☐ pH of amphiprotic salt (initial $\gg K_a$)
- ☐ pH of very dilute solutions
- ☐ Polyprotic acid/base, its pH and concentrations of other solute species
- ☐ Buffer solution

Next, we calculate the pH change of a buffered solution by adding a base.

Example 6G.2 Adding 1.2 g NaOH (0.030 mol) to 500. mL of a buffer solution that is 0.040 M NaCH₃CO₂(aq) and 0.080 M CH₃COOH(aq)

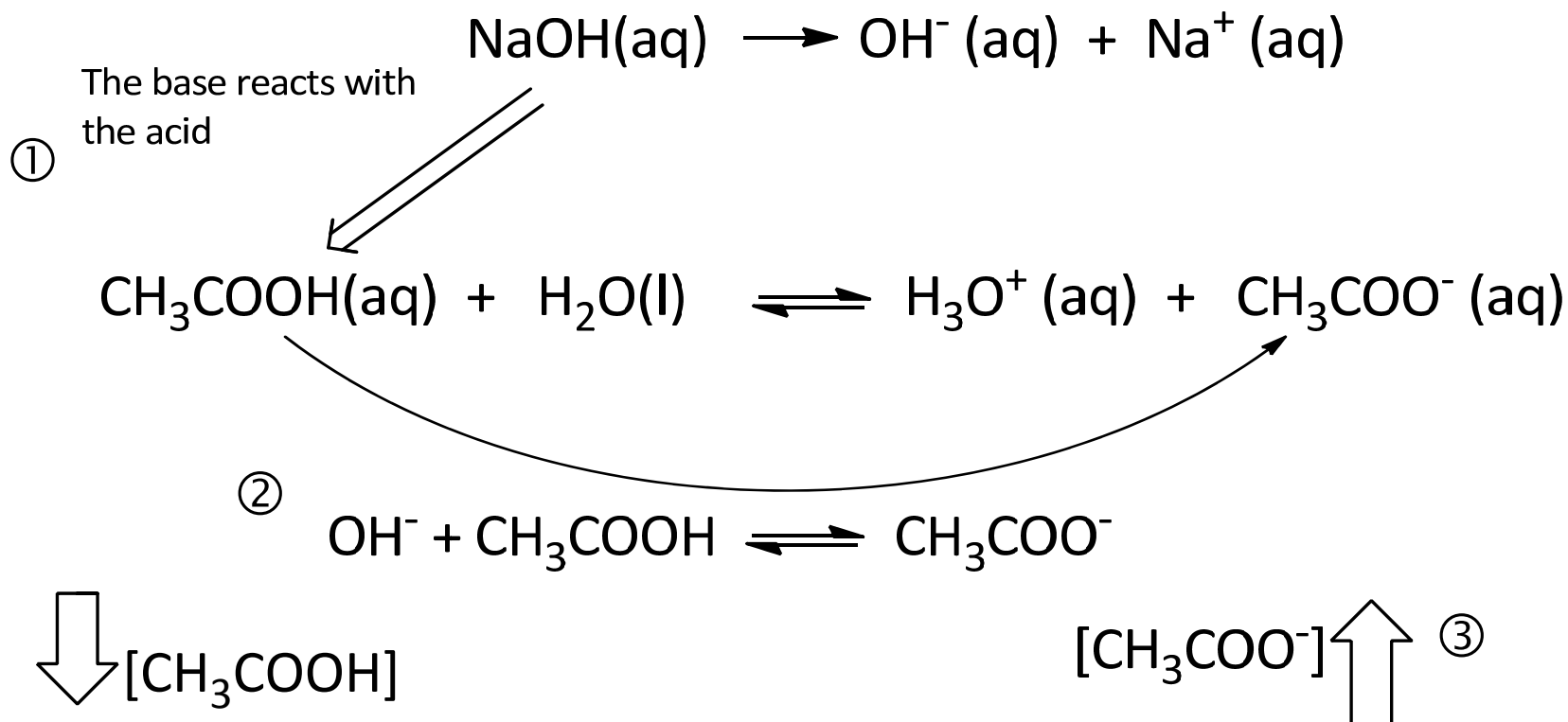


This time we're spiking the buffer with base.

The key point now is to remember that a **strong base** reacts completely with a **weak acid**.

In pure water, adding 1.2 g NaOH produces 0.030 mol OH⁻, and in 500. mL is a 0.060 M OH⁻. The pH: pOH = -log (0.060) = 1.22, or a pH 12.78.

When working with buffers, remember the conjugates pairs



NaOH is removed, and replaced with $\text{CH}_3\text{COO}^{-}$!

1. The OH^{-} from the NaOH reacts with the CH_3COOH ;
2. This produces more conjugate base, $\text{CH}_3\text{COO}^{-}$;
3. What happened—a **strong base is Replaced with a weak base.**

Now adding a base reacts with the acid.

Adding 1.2 g NaOH (0.030 mol) to 500. mL of a buffer solution, we realize that $\text{OH}^- + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^-$ reacts first.

We set up an ICE table that shows the reaction between the strong base and weak acid—these must be in moles since we're showing a reaction.

$$\frac{0.080 \text{ mol acid}}{1 \text{ L}} \times \frac{0.500 \text{ L}}{1} = 0.040 \text{ mol acid}$$

$$\frac{0.040 \text{ mol acetate}}{1 \text{ L}} \times \frac{0.500 \text{ L}}{1} = 0.020 \text{ mol acetate}$$

	CH_3COOH	OH^-	CH_3COO^-
initial	0.040 mol	0.030 mol	0.020 mol
change	-0.030 mol	-0.030 mol	+0.030 mol
equilibrium	0.010 mol	0	0.050 mol

Convert moles to molarity.

$$\frac{0.010 \text{ mol acid}}{1} \times \frac{1}{0.500 \text{ L}} = 0.020 \text{ M acid}$$

$$\frac{0.050 \text{ mol acetate}}{1} \times \frac{1}{0.500 \text{ L}} = 0.10 \text{ M acetate}$$

	CH ₃ COOH	OH ⁻	CH ₃ COO ⁻
initial	0.040 mol	0.030 mol	0.020 mol
change	-0.030 mol	-0.030 mol	+0.030 mol
equilibrium	0.010 mol	0	0.050 mol

Recalculate
the new pH.

	CH ₃ COOH	H ₃ O ⁺	CH ₃ COO ⁻
initial	0.020	0	0.10
change	-x	+x	+x
equilibrium	0.020	x	0.10

$$\text{Solving } K_a = 1.8 \times 10^{-5} = \frac{(0.10)x}{0.020}, \quad x = 3.6 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

using $\text{pH} = -\log [\text{H}_3\text{O}^+]$, $\text{pH} = -\log [3.6 \times 10^{-6}] = 5.44$

$\Delta\text{pH} = 5.44 - 4.44 = 1.0$, which is a much **less dramatic** increase in pure water from $12.78 - 7.00 = 5.78$ pH increase. **And** the strong base is gone, leaving only the weak base.

To prepare a buffer, match the pH to the pK_a or pOH to the pK_b .

Typically, a buffer is made of equal concentrations of both the conjugate acid and base, this is called **equimolar**.

Since $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$ and being equimolar in conjugate acid base, $[HA] = [A^-]$,

Then $[H_3O^+] = K_a$, which means $pH = pK_a$.

For example, if you wanted a buffer solution close to a pH of 5 you would choose the acetic/acetate buffer.

Acid Buffer	pK_a
$HC_2H_3O_2/C_2H_3O_2^-$	4.75
HNO_2/NO_2^-	3.37
$HClO_2/ClO_2^-$	2.00

Quick pH Buffer Approximations: Henderson-Hasselbalch

For any weak acid $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

the equation is rearranged into $[\text{H}_3\text{O}^+] = K_a \underbrace{\frac{[\text{HA}]}{[\text{A}^-]}}$

From $\log x - \log (1/x)$,

Henderson-Hasselbalch: $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]_{\text{intial}}}{[\text{acid}]_{\text{intial}}}$

Example 6G.3 Calculate the ratio of the molarities of CO_3^{2-} and HCO_3^- ions required to achieve buffering at $\text{pH} = 9.50$. The $\text{pK}_{\text{a}2}$ of H_2CO_3 is 10.25.

Using the Henderson-Hasselbalch form: $\text{pH} = \text{pK}_{\text{a}} + \log \frac{[\text{base}]_{\text{initial}}}{[\text{acid}]_{\text{initial}}}$

$$9.50 = 10.25 + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 9.50 - 10.25 = -0.75 \text{ take } 10^x \text{ (antilog) of both sides}$$

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10^{-0.75} = 0.18, \text{ this is the ratio or also written as } \frac{0.18}{1},$$

which means $[\text{CO}_3^{2-}] = 0.18 \text{ M}$, and $[\text{HCO}_3^-] = 1.00 \text{ M}$.

Buffer Capacity

Just as a sponge can hold only so much water, a buffer can mop up only so many hydronium ions.

Buffer capacity is the maximum amount of acid or base that can be added before the buffer loses its ability to resist large changes in pH.

Adding excess acid will overwhelm the conjugate base, or adding too much excess base will overwhelm the conjugate acid.

Buffer Capacity

Broadly speaking, a buffer is found experimentally to have a high capacity for acid when the amount of base present is at least 10% of the amount of acid; similarly for a base.

Experimentally, a buffer works best when it is ± 1 pH range of the pK_a of the buffer solution.
(This comes from the 10% estimation)

Titration

We saw titration in Section L, involving adding a solution, called the titrant, from a buret to a flask containing the sample, called the analyte.

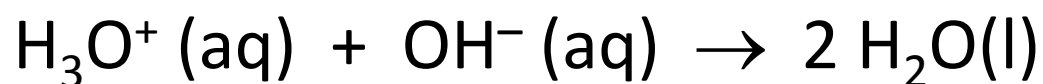
Upon reaching the stoichiometric point, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, the indicator changed color.

We continue using this technique to determine the pH and to select the appropriate indicator.



Strong Acid-Strong Base Titrations

In a neutralization reaction, a strong acid mixes with a strong base,



A plot of the pH against the volume of titrant added during a titration is called a **pH curve**.

A strong acid-strong base titration shows at the stoichiometric point a sudden change in pH near 7.

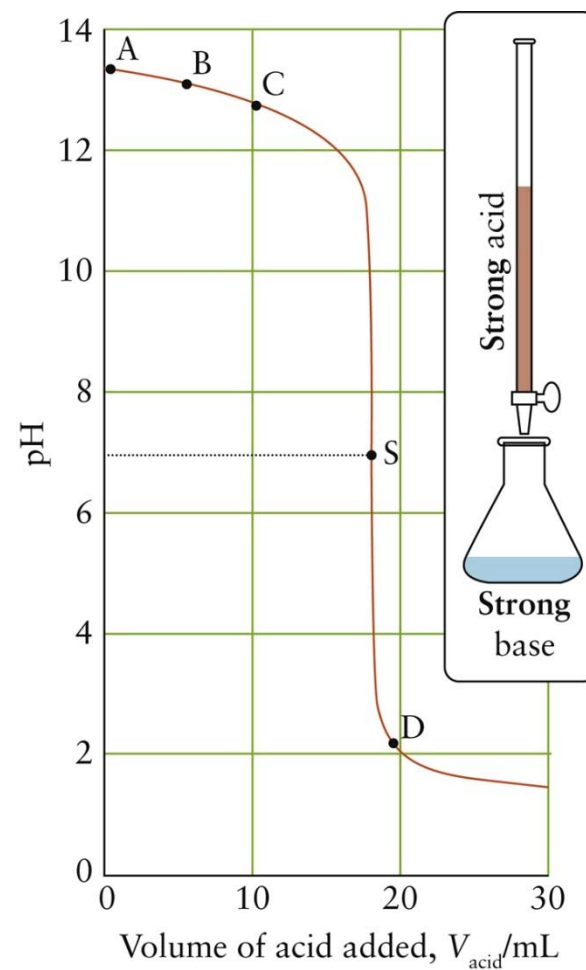


Figure 6H.1
Atkins, *Chemical Principles: The Quest for Insight*, 7e
W. H. Freeman & Company, © 2016 by P. W. Atkins, L. L. Jones, and L. E. Laverman

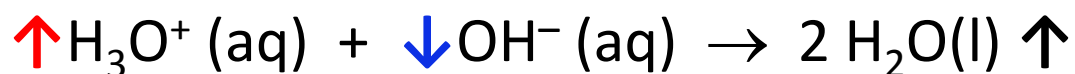
Strong Acid-Strong Base Titrations: Calculations

- Determine the **moles** of acid or base needed;
- Write the neutralization reaction;
- Calculate the **final concentration** by taking the **moles** calculated divided by the **total volume** (total volume = volume analyte + volume titrant).

Example 6H.1 Suppose we are carrying out a titration in which the analyte initially consists of 25.00 mL of 0.250 M NaOH(aq) and the titrant is 0.340 M HCl(aq). After the addition of 5.00 mL of the acid titrant, we can expect the pH to decrease slightly from its initial value. Calculate the new pH.

Initial $[\text{OH}^-]$, $\text{pH} = -\log 0.250 = 0.602$, $[\text{OH}^-] = 14 - .0602 = 13.40$

$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$ the NIE is



Le Chatelier's principle says an **increase** in acid will cause a **shift** to the reactant side, thereby **removing** base, so the pH will decrease.

Example 6H.1 Suppose we are carrying out a titration in which the analyte initially consists of 25.00 mL of 0.250 M NaOH(aq) and the titrant is 0.340 M HCl(aq). After the addition of 5.00 mL of the acid titrant we can expect the pH to decrease slightly from its initial value. Calculate the new pH. ($\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$)

$$\text{Initial OH}^- \text{ mole, } \frac{0.250 \text{ mol HCl}}{\text{L HCl}} \times \frac{0.02500 \text{ L}}{1} = 0.0063 \text{ mol OH}^-$$

$$\text{Moles H}_3\text{O}^+ \text{ added, } \frac{0.340 \text{ mol HCl}}{\text{L HCl}} \times \frac{0.00500 \text{ L}}{1} = 0.0017 \text{ mol H}_3\text{O}^+$$

A strong acid will react completely with a strong base or 0.0063 mol OH^- – 0.0017 mol H_3O^+ = 0.0046 mol OH^- remain.

The new volume is 25.00 mL of basic solution + 5.00 mL of H_3O^+ = 30.00 mL or 0.03000 L total.

$$\text{New concentration of } [\text{OH}^-] = \frac{0.0046 \text{ mol OH}^-}{0.03000 \text{ L OH}^-} = 0.152 \text{ M or pH} = 13.18$$

$$\text{pH} + \text{pOH} = 14, \text{ so pH} = 13.18 \text{ and } \Delta\text{pH} = 13.40 - 13.18 = 0.22$$