

Chapter 9 - Monoprotic Acid-Base

Equilibria *Continued*

Acid/Base Strength

Strong acids and bases **COMPLETELY** dissociates



(No reverse arrow as no HCl present in solution)

Weak acids and bases:

PARTIAL dissociation



acid dissociation constant



base hydrolysis constant

How do you determine the pH of a weak acid or base solution?

Using the systematic treatment of equilibrium:



2. Charge balance - $[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$

3. Mass balance - $F = [\text{A}^-] + [\text{HA}]$

Where F is the formal concentration (total moles of comp'd dissolved per liter)

4. Equilibria - $K_a = [\text{H}^+] [\text{A}^-] / [\text{HA}]$

$$K_w = [\text{H}^+] [\text{OH}^-]$$

5. # of unknowns and equations: $[\text{HA}]$, $[\text{A}^-]$, $[\text{H}^+]$, $[\text{OH}^-]$
and 4 equations.

6. Solve

Assumptions (that come from chemical intuition):

- Assume that most of the $[H^+]$ is coming from the weak acid and not from the water dissociation. (so this $HA \Leftrightarrow H^+ + A^-$ predominant over this $H_2O \Leftrightarrow H^+ + OH^-$).
- With this assumption, $[H^+] \approx [A^-]$.

So..

If we let $x = [H^+] = [A^-]$, then $[HA] = F - x$ (Recall, F is the molarity of HA added to solution, so we subtract the molarity of HA that has dissociated to H^+ and A^- to get the $[HA]$ in solution.)

$$K_a = [H^+] [A^-] / [HA] = x^2 / (F - x)$$

Example:

What is the pH of a solution of 0.030 M formic acid?

$K_a = 1.80 \times 10^{-4}$ of formic acid.



Determining pH of weak base:

Similar for base

If we let $x = [\text{OH}^-] \approx [\text{BH}^+]$, then $[\text{B}] = F - x$ (Recall, F is the molarity of B added to solution, so we subtract the molarity of B that has dissociated to OH^- and BH^+ to get the $[\text{B}]$ in solution.)

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{(F - x)}$$

Example:

What is the pH of a 0.030 M Pyridine? $K_b = 1.7 \times 10^{-9}$

Fraction of Dissociation of acid or base:

For an acid -

$$\begin{aligned}\alpha &= [A^-] / ([A^-] + [HA]) \\ &= x / (x + (F - x)) = x / F\end{aligned}$$

where $x = [A^-] = [H^+]$

and $F = \text{initial concentration of HA}$

Or $\alpha = \text{concentration of A}^- / \text{initial concentration of HA}$

For a base -

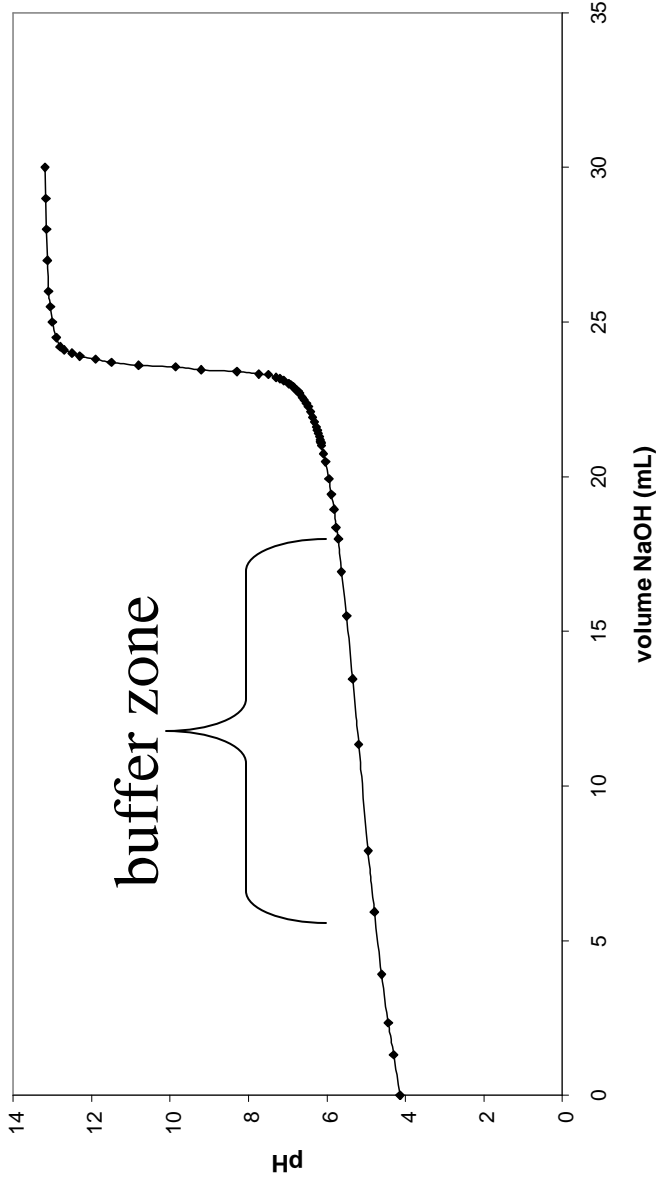
$$\begin{aligned}\alpha &= [BH^+] / ([BH^+] + [B]) \\ &= x / (x + (F - x)) = x / F\end{aligned}$$

where $x = [BH^+] = [OH^-]$

$F = \text{initial concentration of base [B]}$

Buffer

- A buffer solution resists changes in pH when acids or bases are added or when dilution occurs.
- If buffering was not possible, we would have acid/base problems in biological systems, environmental systems, etc.



What is a buffer?



If we add both the acid (HA) and its conjugate base to the solution (A^-) to the solution, then....

- the added A^- or H^+ , the acid reaction goes to the right:
- the added HA or OH^- , the base reaction goes to the right:



The net result is that neither the acid or the base will increase H^+ or OH^- content, so the pH (and pOH) will not change.

Henderson-Hasselbalch Equation

Describes the pH of a solution from the pK_a and the ratio of the concentrations of the acid and its conjugate base.

$$\text{pH} = \text{p}K_a + \log \left[\frac{[A^-]}{[HA]} \right]$$

You can prepare a buffer with a base and its conjugate acid so...

For solution prepared from a weak base:

$$\text{pH} = \text{p}K_a + \log \left[\frac{[B]}{[BH^+]}\right]$$

However, most buffers are made from an acid and its conjugate base.

Things to notice about the Henderson-Hasselbalch Equation:

When the $[\text{base}] = [\text{acid}]$, then

$$\text{pH} = \text{pK}_a + \log [\text{base}] / [\text{acid}]$$

$$\text{pH} = \text{pK}_a + \log 1$$

So... $\text{pH} = \text{pK}_a$

When the $[\text{base}] \neq [\text{acid}]$, then the $\text{pH} \neq \text{pK}_a$

$[\text{base}] / [\text{acid}]$	$\log [\text{base}] / [\text{acid}]$	pH
100:1	$\log(100) = 2$	$\text{pK}_a + 2$
10:1	$\log(10) = 1$	$\text{pK}_a + 1$
1:10	$\log(0.1) = -1$	$\text{pK}_a - 1$
1:100	$\log(0.01) = -2$	$\text{pK}_a - 2$

Buffer Capacity (β)

Describes how well a solution resists changes in pH when a strong acid or strong base is added.

$\beta = dC_b / dpH$ for addition of base

$\beta = dC_a / dpH$ for addition of acid

In words:

The larger the buffer capacity, the higher the concentration of strong acid or strong base you can add without affecting the pH. The largest buffer capacity is when $pH = pK_a$. So..

Choose the acid or base for buffering that has a pK_a at or near the desired pH.

Making a Buffer

1. Determine the desired pH.
2. Choose an acid or base with a pK_a near the desired pH (See Table 10-2 for list of commonly used buffers).
3. Decide on the concentration (common concentration is 0.1M).
4. Make up solution using normal procedures except only add approximately $\frac{3}{4}$ the need volume of water.
5. Use a strong acid or strong base to adjust the pH to the desired pH value (should be near the pK_a) value using a pH meter to determine the pH of the solution.
6. After the pH adjustment is made, then finish dilution of solution.

This approach is better than calculating the amount of acid or base needed since activities, temperature, etc. can alter pH.

Summary of Buffers

- Buffers are a mix of a weak acid and its conjugate base (typically).
- Buffers are best when the desired $\text{pH} \approx \text{pK}_a$ of the acid.
- Over a fairly large range of concentrations, the pH of a buffer is independent of concentration.
- A buffer resists changes in pH when an acid or base is added to solution (its purpose in the chemical world!).
- If a lot of acid or base is added, then the buffer will give way to pH changes (nothing is perfect).

What is the ratio of $[\text{HNO}_2] / [\text{NO}_2^-]$ in a solution of NaNO_2
($\text{pK}_b 10.85$) at:

a) pH 2

b) pH 10