

Monoprotic Acid/Base Equilibria

Strong acids and bases:

What is the pH of 0.10 M HCl? How do you calculate it? Why?

Concentration (F)	pH
0.10 (10^{-1})	
0.01 (10^{-2})	
0.001 (10^{-3})	
0.0001 (10^{-4})	
0.00001 (10^{-5})	
0.000001 (10^{-6})	
0.0000001 (10^{-7})	
0.00000001 (10^{-8})	

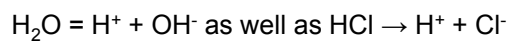
Based on our typical method for calculating pH, at 10^{-8} M HCl, pH is greater than 7.00, does this make sense?

Where have we gone wrong?

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Monoprotic Acid/Base Equilibria

We have to consider autoprotolysis of water:



Charge Balance:

Mass Balance:

So:

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Autoprotolysis

Question: When do we have to be concerned with autoprotolysis?

Answer: When the (strong) acid or base concentration is around $K_w^{1/2}$ ($\sim 10^{-6}$ to 10^{-8} F).

Why not just when the concentration is $< 10^{-6}$ F?

Lets look back at our strong acid calculation (charge balance)

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

as [Strong Acid] gets smaller and smaller, $[\text{OH}^-]$ approaches $[\text{H}^+]$

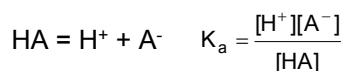
So, for extremely low strong acid or base concentration ($< 10^{-8}$ F),
pH = 7.00

Problem: What is the pOH, and pH of a 2.48×10^{-7} F solution of NaOH?

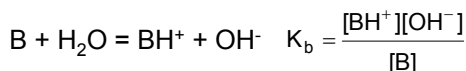
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Weak Acids and Bases: Quick Review

Acid Dissociation:



Base Hydrolysis:



For any conjugate acid base pair

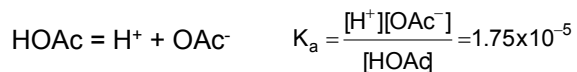
$$K_a K_b = K_w$$

What is the pH of a solution prepared by dissolving 0.10 moles of acetic acid in 1.00 L solution? This is tougher than it sounds!

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pH of a Weak Acid Solution

What is the pH of a solution prepared by dissolving 0.10 moles of acetic acid in 1.00 L solution? This is tougher than it sounds!



Charge Balance:

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

Mass Balance:

$$[\text{HOAc}] + [\text{OAc}^-] = 0.10 \text{ F}$$

Four unknowns, four equations, time to solve.

We end up with a third order equation! What to do?!?

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pH of a Weak Acid Solution

Let's make a simplifying approximation.

- Since HOAc is a much stronger acid than H₂O (look at the K_a's), the overwhelming majority of the protons in solution will come from the dissociation of HOAc
- Every time a proton (H⁺) is liberated, an acetate (OAc⁻) is liberated as well
- So, [H⁺] ≈ [OAc⁻], and therefore, [OH⁻] << [OAc⁻]

What does that do for us?

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pH of a Weak Acid Solution

We can make this simplifying assumption ($[H^+] \approx [A^-]$) for any weak acid equilibrium (**as long as we verify it at the end**) this will always lead to the following equation:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F-x}$$

where $x = [H^+]$.

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pH of a Weak Acid Solution

This equation can be solved using the quadratic formula, BUT:

In some instances, we can make things easier yet:

- Remember, HA is a weak acid, so it only dissociates slightly (the K_a equilibrium lies to the left b/c $K_a \ll 1$)
- So, [HA] at equilibrium will not vary much from its initial value, as long its initial concentration (F) isn't extremely dilute.
- This allows us to approximate F-x as F, the equation now becomes:

$$K_a = \frac{x^2}{F} \quad \text{or} \quad x = \sqrt{K_a F}$$

- This approximation is usually good as long as $K_a < 0.01F$ ****

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Fraction of Dissociation

Just how much (what fraction) HA dissociates? It depends on a couple of things:

1.

2.

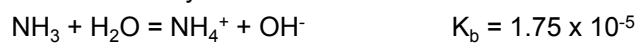
To calculate fraction of dissociation, α , for a monoprotic weak acid:

This reduces to:

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pH of a Weak Base Solution

The process is basically the same.



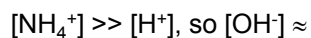
What is the pH of 0.025 F ammonia?

Equilibrium Constants:

Charge Balance:

Mass Balance:

Simplifying assumption:



Simplified solution:

What is the fraction of association of ammonia under these conditions?

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Conjugate Acid-Base Pairs and Buffers

Items to remember about conjugate acid-base pairs:

- The conjugate acid of a weak base is a weak acid and the conjugate base of a weak acid is a weak base.
- For any conjugate acid-base pair, $K_a K_b = K_w$, where K_a is the acid dissociation constant for the weak acid, and K_b is the base hydrolysis constant for the conjugate base.
- Therefore, the conjugate base of a moderately weak acid is a stronger base than the conjugate of a very weak acid:

$$\text{If } K_{a1} > K_{a2}, K_{b1} < K_{b2}$$

Buffers: What is a buffer?

Why would you ever need a buffer?

How does a buffer work?

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Buffer pH and the Henderson-Hasselbach Equation

H-H Relates pH to relative equilibrium concentrations of acid and conjugate base in solution.

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

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Buffer pH and the Henderson-Hasselbach Equation

We use the H-H equation to predict pH using non-equilibrium concentrations. How can we get by not accounting for dissociation?

To a first approximation, the pH of a buffer is essentially independent of dilution. Why?

What you mix isn't exactly what you get, Why?

- Activity and ionic strength considerations
- Concentrations of HA and A⁻ may not be equal to their formalities
- Dilute solutions, extreme pH

Critical Consideration: How would you prepare a buffer solution?

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Buffer Behavior and Selection

Buffer Capacity:

$$\beta = \frac{dC_b}{dpH} = -\frac{dC_a}{dpH}$$

- Buffer capacity is a maximum when pH = pK_a
- Best to choose a buffer system whose pK_a is within ±1 pH unit of your desired pH (b/c capacity diminishes greatly outside this range).

PROBLEMS:

1. Calculate the pH of a solution prepared by mixing 0.010 mol of acetic acid with 0.010 mol of sodium acetate in 1.0 L solution.
2. Calculate the new pH of this buffer after the addition of 15 mL of 0.100 F NaOH.
3. Would you expect a larger or smaller pH change if the buffer had been prepared from 0.10 mol HOAc and 0.10 mol NaOAc? Verify your prediction with a calculation.

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