

Monoprotic Acid/Base Equilibria

Strong acids and bases:

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

$-\log [H^+] = pH$

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

WTF? {

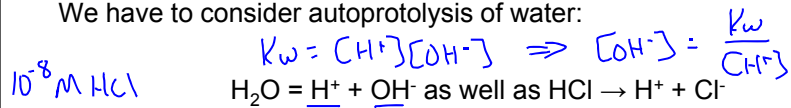
Based on our typical method for calculating pH, at 10^{-8} M HCl, pH is greater than 7.00, does this make sense?

Where have we gone wrong?

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Monoprotic Acid/Base Equilibria

We have to consider autoprotolysis of water:



Charge Balance: $[H^+] = [OH^-] + [Cl^-]$

Mass Balance: ~~$[H^+] = [OH^-] + [Cl^-]$~~

So:

$$[Cl^-] = 10^{-8} M \quad [H^+] = 1.05 \times 10^{-7} M$$

$$[H^+] = \frac{K_w}{[H^+]} + 10^{-8} M \quad = 9.51 \times 10^{-8} M$$

$$[H^+] = 1.05 \times 10^{-7} M$$

$$pH = 6.98$$

$$[H^+]^2 = K_w + 10^{-8}[H^+]$$

$$[H^+]^2 - 10^{-8}[H^+] - K_w = 0$$

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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).

$$\frac{[\text{Acid}]}{[\text{Base}]} < 10^8 \text{ M}, \text{ pH} \approx 7.00$$

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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$$2.48 \times 10^{-7} \text{ M NaOH}$$



$$\text{C.B.} \rightarrow [\text{H}^+] + [\text{Na}^+] = [\text{OH}^-]$$

$$\text{M.B.} \rightarrow [\text{Na}^+] = 2.48 \times 10^{-7} \text{ M}$$

$$[\text{H}^+] = 3.53 \times 10^{-8} \text{ M},$$
~~$$- 2.83 \times 10^{-7} \text{ M}$$~~

$$[\text{H}^+] + 2.48 \times 10^{-7} \text{ M} = \frac{K_w}{[\text{H}^+]}$$

$$[\text{H}^+]^2 + 2.48 \times 10^{-7} [\text{H}^+] - K_w = 0$$

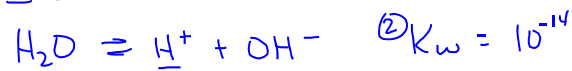
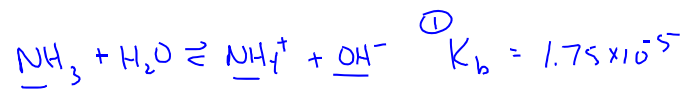
$$\text{pH} = 7.45$$

$$\text{pOH} = 6.55$$

$$\text{pH} + \text{pOH} = 14$$

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$$2.48 \times 10^{-7} \text{ M } \text{NH}_3$$



$$\text{C.B. } \textcircled{3} \quad [\text{NH}_4^+] + [\text{H}^+] = [\text{OH}^-] \quad \text{C.B. } [\text{NH}_4^+] + [\text{H}^+] - [\text{OH}^-] = 0$$

$$\text{M.B. } \frac{[\text{OH}^-]}{[\text{H}^+]} = \frac{[\text{NH}_4^+] + [\text{H}^+]}{[\text{H}^+]} \quad \frac{K_w}{[\text{H}^+]}$$

$$[\text{NH}_3]_T = ([\text{NH}_3] + [\text{NH}_4^+]) = 2.48 \times 10^{-7} \text{ M}$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad [\text{NH}_4^+] = f([\text{H}^+], K_b)$$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{2.48 \times 10^{-7} - [\text{NH}_4^+]}$$

$$[\text{NH}_3] = 2.48 \times 10^{-7} - [\text{NH}_4^+]$$

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$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{2.48 \times 10^{-7} \text{ M} - [\text{NH}_4^+]}$$

$$2.48 \times 10^{-7} K_b - K_b [\text{NH}_4^+] = [\text{NH}_4^+][\text{OH}^-]$$

$$2.48 \times 10^{-7} K_b = [\text{NH}_4^+][\text{OH}^-] + K_b [\text{NH}_4^+]$$

$$[\text{NH}_4^+] = \frac{2.48 \times 10^{-7} K_b}{[\text{OH}^-] + K_b} = \frac{2.48 \times 10^{-7} K_b}{K_w/[\text{H}^+] + K_b}$$

$$[\text{NH}_4^+] + [\text{H}^+] = [\text{OH}^-]$$

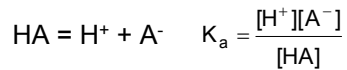
$$\frac{2.48 \times 10^{-7} K_b}{K_w/[\text{H}^+] + K_b} + [\text{H}^+] = \frac{K_w}{[\text{H}^+]}$$

$$[\text{H}^+]^3 + 2.48 \times 10^{-7} K_b [\text{H}^+]^2 - K_w K_b [\text{H}^+] - K_w^2 = 0$$

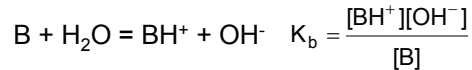
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Weak Acids and Bases: Quick Review

Acid Dissociation:



Base Hydrolysis:



For any conjugate acid base pair

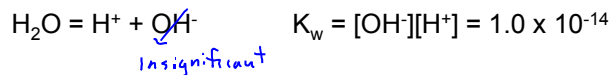
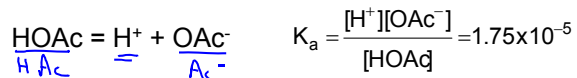
$$K_a K_b = K_w$$

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:

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

OH- 0

Mass Balance:

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

(H+)

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

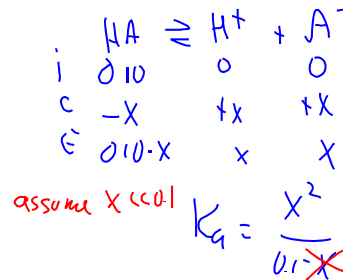
Let's make a simplifying approximation.

- 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?

$$K_a = \frac{[H^+]^2}{0.10 - [H^+]}$$

$$[H^+] = \sqrt{0.10 K_a}$$



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pH of a Weak Acid Solution

We can make this simplifying assumption ([H⁺] ≈ [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:

$$K_a \downarrow \quad x \downarrow \quad x \ll F \quad F \uparrow$$

$$[H^+] \ll F$$

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 $K_a < 0.01F$

$$F > 100 K_a$$

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$$K_a = \frac{x^2}{0.1 - x} \quad 0.1 K_a - K_a x = x^2$$

$$x^2 + K_a x - 0.1 K_a = 0$$

$$[H^+] = \sqrt{K_a F}$$

$$= \sqrt{1.75 \times 10^{-5} \cdot 0.1}$$

$$pH = 2.878$$

① ignore H_2O , $pH = 2.881 = 2.88$
Solve quadratic

② ①, recognize $[HA]_{eq} \approx [HA]_i$
 $pH = 2.878 = 2.88$

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$HA \rightleftharpoons H^+ + A^-$ **Fraction of Dissociation** $K_a = \frac{[H^+][A^-]}{[HA]}$

Association

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

- K_a (acid strength)
- pH

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

$$\alpha = \frac{[A^-]}{[HA] + [A^-]} = \frac{\frac{K_a[HA]}{[H^+]}}{[HA] + \frac{K_a[HA]}{[H^+]}} = \frac{\frac{K_a}{[H^+]}}{1 + \frac{K_a}{[H^+]}} = \frac{K_a}{K_a + [H^+]}$$

This reduces to:

$0 \leq \alpha \leq 1$

$\alpha = \frac{K_a}{K_a + [H^+]}$ $\alpha \approx \frac{K_a}{K_a} = 1$ (in basic $[H^+] \downarrow$)

$\alpha_{HA} = 1 - \alpha_{A^-}$

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$NH_3 \rightleftharpoons NH_4^+ + OH^-$

(0.025 M) (-x) (+x) (+x)

pH of a Weak Base Solution

The process is basically the same.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $K_b = 1.75 \times 10^{-5}$

What is the pH of 0.025 M ammonia?

Equilibrium Constants:

Charge Balance:

Mass Balance:

Simplifying assumption:

$[NH_4^+] \gg [H^+]$, so $[OH^-] \approx [NH_4^+]$

Simplified solution: $[OH^-] = 6.7 \times 10^{-4} M$ $pH = 10.83$

"x" = $[OH^-]$, $[NH_4^+]$

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

$\alpha_{NH_4^+} = \frac{[NH_4^+]}{[NH_3] + [NH_4^+]} = \frac{6.7 \times 10^{-4}}{0.025} = 2.68\%$

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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:

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

Buffers: What is a buffer? *Resists change in pH.
Contains weak acid / conj. base pair.*

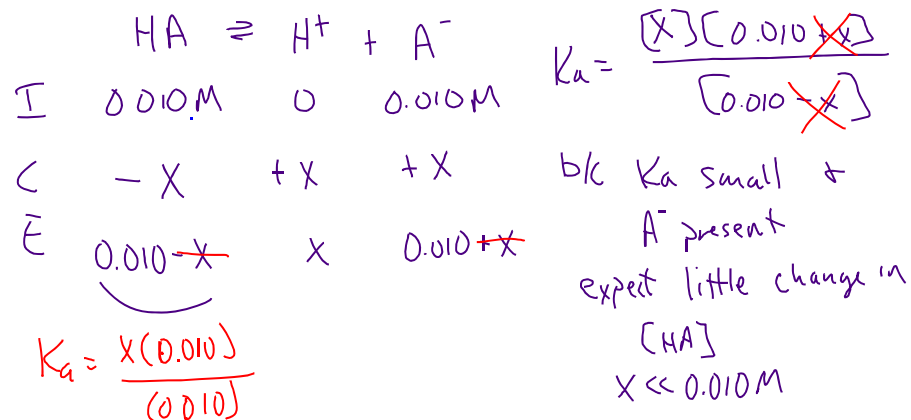
Why would you ever need a buffer?

How does a buffer work?

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$$K_a = 1.75 \times 10^{-5} \quad pK_a = 4.75 \quad \text{Buffer pH}$$

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.



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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.

$$pH = f(K_a, [A^-]/[HA])$$

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

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

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

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

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

1 mol HA, 1 mol A⁻ in 100 mL
 $pH = pK_a + \log \frac{[A^-]}{[HA]}$
 dilute to 1 L
 $pH = ?$

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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?

dangerous @ low F of either HA and/or A⁻

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

Ratio of A⁻/HA

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:

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

$$\begin{aligned} pH &= pK_a && \text{mol A}^- / \text{mol HA} \\ pH &= pK_a + 1 && 10 \\ pH &= pK_a - 1 && 0.10 \\ pH &= pK_a + \log \frac{\text{mol A}^-}{\text{mol HA}} \end{aligned}$$

- 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. $pH = pK_a$
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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$pK_a = 4.75$, 0.010 mol HA, 0.010 mol A^- , 15 mL 0.1 F NaOH
1.5 mmol

PH?

	$HA + NaOH \rightarrow NaA + H_2O$			
Start	10 mmol	1.5 mmol	10 mmol	—
End	8.5 mmol	0	11.5 mmol	

$pH = pK_a + \log \frac{\text{mmol } A^-}{\text{mmol HA}}$

$4.88 = 4.75 + \log \frac{11.5 \text{ mmol}}{8.5 \text{ mmol}}$

Start	100 mmol	1.5 mmol	100 mmol	$4.76 = 4.75 + \log \frac{101.5}{98.5}$
End	98.5 mmol	0	101.5 mmol	

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pH 7.00 phosphate buffer, 0.10M assume 1L

$$\text{H}_3\text{PO}_4 \xrightleftharpoons[\text{pK}_1]{K_{a1}} \text{H}_2\text{PO}_4^- \xrightleftharpoons[\text{pK}_2]{K_{a2}} \text{HPO}_4^{2-} \xrightleftharpoons[\text{pK}_3]{K_{a3}} \text{PO}_4^{3-}$$

$\text{pK}_1 = 1.91$, $\text{pK}_2 = 5.00$, $\text{pK}_3 = 6.71$, 11.52

$\text{H}_3\text{PO}_4, \text{NaH}_2\text{PO}_4, \text{Na}_2\text{HPO}_4, \text{Na}_3\text{PO}_4$

$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$

Prepare using $\text{NaH}_2\text{PO}_4 / \text{Na}_2\text{HPO}_4$

$$7.00 = 6.71 + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$\log \frac{\text{mol A}^-}{\text{mol HA}} = 7.00 - 6.71 = 0.29$$

$$\frac{\text{mol A}^-}{\text{mol HA}} = 10^{0.29} = 1.95$$

$1.95 \text{ mol HA} + \text{mol HA} = 0.1 \text{ mol}$

$$\text{mol HA} = \frac{0.1}{2.95}$$

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$\text{pK}_a = 2$

$$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_2\text{P}_4^-$$

$\text{pH} = \text{pK}_a + \log \frac{\text{mol A}^-}{\text{mol HA}}$

$$5.00 = 2 + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$3 = \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$\frac{\text{mol A}^-}{\text{mol HA}} = 10^3$$

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