Monoprotic Acid/Base Equilibria

Strong acids and bases:

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

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

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:

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

10^{-8} M HCl

$H_2O = H^+ + OH^-$ as well as $HCl \rightarrow H^+ + Cl^-$

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

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

$[Cl^-] = 10^{-8}$ M

So:

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

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

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

$[H^+] = 1.05 \times 10^{-7}$ M, ~~-9.51×10^{-8} M~~

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

pH = 6.98

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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 $K_w^{1/2}$ (~10^{-6} to 10^{-8} F). $[Acid]$ $[Base]$ $< 10^{-8} M$, $pH \approx 7.00$

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

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

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

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

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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$2.48\times10^{-7} M$ NaOH

$NaOH \rightarrow Na^+ + OH^-$

$H_2O \rightleftharpoons H^+ + OH^- \rightarrow K_w = [H^+][OH^-]$

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

M.B. $\rightarrow [Na^+] = 2.48\times10^{-7} M$

$[H^+] + 2.48\times10^{-7} M = \frac{K_w}{[H^+]}$

$[H^+]^2 + 2.48\times10^{-7}[H^+] - K_w = 0$

$[H^+] = 3.53\times10^{-8} M$, ~~$-2.83\times10^{-7} M$~~

pH = 7.45

pOH = 6.55

pH + pOH = 14

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2.48×10^{-7} M NH_3

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (1)\ K_b = 1.75\times10^{-5}$$

$$H_2O \rightleftharpoons H^+ + OH^- \quad (2)\ K_w = 10^{-14}$$

C.B. (3) $[NH_4^+] + [H^+] = [OH^-]$ ← $\frac{K_w}{[H^+]}$ $\quad [NH_4^+] + [H^+] - [OH^-] = 0$

M.B. ~~$[OH^-] = [NH_4^+] + [H^+]$~~

(4) $["NH_3"]_T = [NH_3] + [NH_4^+] = 2.48\times10^{-7}$ M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad [NH_4^+] = f([H^+], K_i's)$$

$$[NH_3] = 2.48\times10^{-7} - [NH_4^+]$$

$$K_b = \frac{[NH_4^+][OH^-]}{2.48\times10^{-7} - [NH_4^+]}$$

$$K_b = \frac{[NH_4^+][OH^-]}{2.48\times10^{-7}M - [NH_4^+]}$$

$$2.48\times10^{-7}K_b - K_b[NH_4^+] = [NH_4^+][OH^-]$$

$$2.48\times10^{-7}K_b = [NH_4^+][OH^-] + K_b[NH_4^+]$$

$$[NH_4^+] = \frac{2.48\times10^{-7}K_b}{[OH^-] + K_b} = \frac{2.48\times10^{-7}K_b}{K_w/[H^+] + K_b}$$

$$[NH_4^+] + [H^+] = [OH^-]$$

$$\frac{2.48\times10^{-7}K_b}{K_w/[H^+] + K_b} + [H^+] = \frac{K_w}{[H^+]}$$

$$[H^+]^3 + 2.48\times10^{-7}K_b[H^+]^2 - K_wK_b[H^+] - K_w^2 = 0$$

Weak Acids and Bases: Quick Review

Acid Dissociation:

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

Base Hydrolysis:

$B + H_2O = BH^+ + OH^-$ $\quad K_b = \frac{[BH^+][OH^-]}{[B]}$

For any conjugate acid base pair

$$K_aK_b = K_w$$

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!

$HOAc = H^+ + OAc^-$ $\quad K_a = \frac{[H^+][OAc^-]}{[HOAc]} = 1.75\times10^{-5}$

HAc = Ac⁻

$H_2O = H^+ + OH^-$ $\quad K_w = [OH^-][H^+] = 1.0 \times 10^{-14}$

insignificant

Charge Balance:

$$[H^+] = [OH^-] + [OAc^-]$$

0

Mass Balance:

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

$[H^+]$

$[H^+] = 0.10F - [HOAc]$

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 H_2O (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, $[H^+] \approx [OAc^-]$, and therefore, $[OH^-] << [OAc^-]$

What does that do for us?

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

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

	HA	⇌	H^+	+	A^-
i	0.10		0		0
c	$-x$		$+x$		$+x$
E	$0.10-x$		x		x

assume $x << 0.1$

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

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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:

$K_a \downarrow$ $x \downarrow$ $F \uparrow$ $x \ll F$ $[H^+] \ll F$

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

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

$$[H^+] = \sqrt{K_a F} = \sqrt{1.75 \times 10^{-5} \cdot 0.1}$$

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

Association

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

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

1. K_a (acid strength)
2. pH

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

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:

$0 \leq \alpha \leq 1$

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

in basic $[H^+]\downarrow$

$\alpha \approx \frac{K_a}{K_a} \approx 1$

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

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

	NH_3	NH_4^+	OH^-
I	0.025	0	0
C	$-x$	$+x$	$+x$

pH of a Weak Base Solution

The process is basically the same.

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

What is the pH of 0.025 F ammonia?

Equilibrium Constants:

Charge Balance:

Mass Balance:

Simplifying assumption:

$[NH_4^+] >> [H^+]$, 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, $K_aK_b=K_w$, where K_a is the acid dissociation constant for the weak acid, and K_b is the base hydrolysis constant for the conjugate base.
- There for, the conjugate base of a moderately weak acid is a stronger base than the conjugate of a very weak acid:

If $K_{a1} > K_{a2}$ $K_{b1} < K_{b2}$

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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$K_a = 1.75 \times 10^{-5}$ $pK_a = 4.75$

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.

	HA	$\rightleftharpoons$ H^+	+ A^-
I	0.010 M	0	0.010 M
C	$-x$	$+x$	$+x$
E	$0.010 - x$	x	$0.010 + x$

$$K_a = \frac{[x][0.010 + x]}{[0.010 - x]}$$

b/c Ka small & A^- present expect little change in [HA]

$x \ll 0.010 M$

$$K_a = \frac{x(0.010)}{(0.010)}$$

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

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

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

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

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

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

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:

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

pH = pKa
pH = pKa + 1
pH = pKa − 1
$pH = pK_a + \log \frac{mol\ A^-}{mol\ HA}$
mol A⁻/mol HA: 1, 10, 0.10

- Buffer capacity is a maximum when pH = pK_a
- Best to chose 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 = pKa
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	→ NaA	+ H_2O
Start	10 mmol	1.5 mmol	10 mmol	—
End	8.5 mmol	0	11.5 mmol	

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

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

Start	100 mmol	1.5 mmol	100 mmol
End	98.5 mmol	0	101.5 mmol

$4.76 = 4.75 + \log \frac{101.5}{98.5}$

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pH 7.00 phosphate buffer, 0.10 M assume 1L

$H_3PO_4 \underset{1.91}{\overset{K_{a1}}{\rightleftharpoons}} H_2PO_4^- \underset{6.71}{\overset{K_{a2}}{\rightleftharpoons}} HPO_4^{2-} \underset{11.52}{\overset{K_{a3}}{\rightleftharpoons}} PO_4^{3-}$

pK 5.00

mol A^- + mol HA = 0.1 mol

H_3PO_4, NaH_2PO_4, Na_2HPO_4, Na_3PO_4

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

Prepare using NaH_2PO_4 / Na_2HPO_4

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

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

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

mol A^- = 1.95 mol HA

1.95 mol HA + mol HA = 0.1 mol

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

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$H_3PO_4 \overset{pK_a = 2}{\rightleftharpoons} H_2PO_4^-$ mol $H_2PO_4^-$

$pH = pK_a + \log\frac{mol\ H_2PO_4^-}{mol\ H_3PO_4}$

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

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

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

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