"A" students work
(without solutions manual)
~ 10 problems/night.

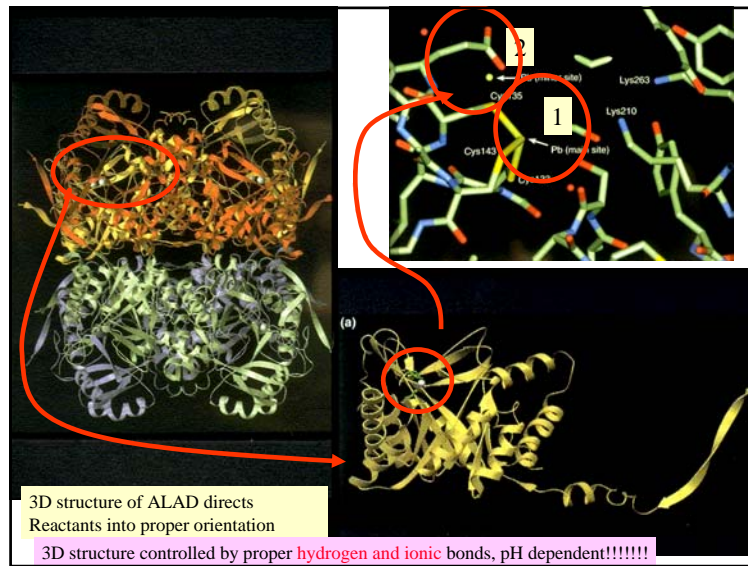Dr. Alanah Fitch
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Office Hours Th&F 2-3:30 pm

Module #17B:
Acid Base Ionization
Computations

To determine if our protein unfolds or not is it sufficient to know the K_a and K_b
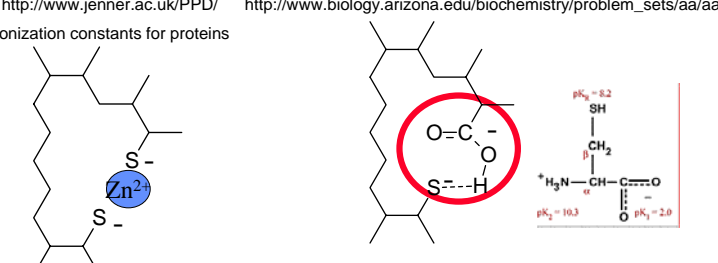Values of the functional groups?

3D structure of ALAD directs
Reactants into proper orientation

3D structure controlled by proper hydrogen and ionic bonds, pH dependent!!!!!!!

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http://www.jenner.ac.uk/PPD/   http://www.biology.arizona.edu/biochemistry/problem_sets/aa/aa.ht
Ionization constants for proteins

$$RCOOH_{aq} + H_2O_\ell \rightleftarrows RCOO^-_{aq} + H_3O^+_{aq}$$

$$RSH_{aq} + H_2O_\ell \rightleftarrows RS^-_{aq} + H_3O^+_{aq}$$

R refers to rest of protein

cysteine

$$K_{a,COOH} = 1.0x10^{-2}$$
$$K_{a,SH} = 6.3x10^{-9}$$

Phosphoenolate carboxylase, human, cys
$$K_a = 7.94x10^{-9}$$

Control of protein shape is due to **fraction** of sites charged

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Slide 1

Protein folding due to FRACTION of sites charged

$K_{a,Val,NH_3} = 2.5 \times 10^{-10}$

$K_{a,Val,COOH} = 5.01 \times 10^{-3}$

$K_{a,tyr,ROH} = 1.0 \times 10^{-10}$

(a) Front view

(b) Side view

Val

Lys 127

Val 34

Cl

β_2

141 Arg

Val 93

α_2 126 Asp

Tyr 140

α_1

Hemeglobin

Slide 2
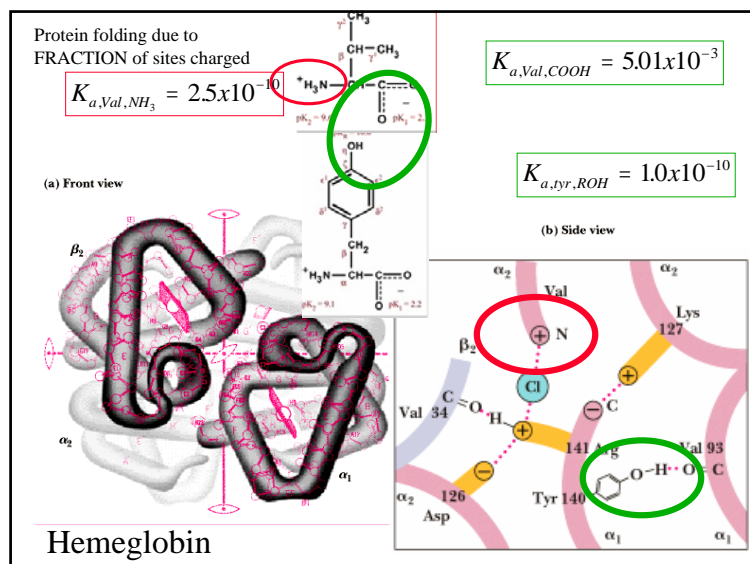
% Ionized (dissociated)

$$HA_{aq} \underset{\leftarrow}{\rightarrow} H_3O^+_{aq,from\ HA} + A^-_{aq}$$

$$\% \, dissociation = 100\left[\frac{amount\ dissociated\ (M)}{initial\ concentration\ (M)}\right]$$

$$\% \, dissociation = 100\left[\frac{\left[A^-_{aq}\right]}{\left[HA_{aq,initial}\right]}\right]$$

This seems pretty straight forward

Slide 3

Calculating [A-]

This will require knowing [$H_3O_{aq}+$]

$$HA_{aq} \underset{\leftarrow}{\rightarrow} H_3O^+_{aq,from\ HA} + A^-_{aq}$$

$$K_a = \frac{\left[A^-_{aq,eq}\right]\left[H_3O^+_{aq,eq}\right]}{\left[HA_{eq,aq}\right]}$$

AND a new vocabulary for comparing the **solution acidity** from experiment to experiment

K_a and K_b tell us about the possibility Of donating protons, not what the solution Acidity is

Define another comparison number: pH

Slide 4

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Module #17B:
Acid Base Ionization Computations

pH, pOH, pKa

I WANT YOU TO PRACTICE EVERY DAY!

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Slide 1

Chemists are LAZY

To shorten calculations use log

$$\log(ab) = \log(a) + \log(b)$$

$$\log\left(\frac{a}{b}\right) = \log(a) - \log(b)$$

$$p[x] \equiv -\log[x]$$

$$\log(a)^x = x\log(a)$$

$$\log\frac{1}{(a^x)} = \log(a^{-x}) = -x\log(a)$$

Slide 2

$$K = \frac{\left[OH^-_{eq}\right]\left[H_3O^+_{eq}\right]}{\left[H_2O\right]^2}$$

Assumption that 55.5 molar is relative unchanged

$$K\left[H_2O\right]^2 = \left[OH^-_{eq}\right]\left[H_3O^+_{eq}\right]$$

$$K[55.55]^2 = \left[OH^-_{eq}\right]\left[H_3O^+_{eq}\right]$$

$$K[55.55]^2 = K_W = 10^{-14}$$

$$K_W = 10^{-14} = \left[OH^-_{eq}\right]\left[H_3O^+_{eq}\right]$$

Slide 3

$$K_W = 10^{-14} = \left[OH^-_{aq}\right]\left[H_3O^+_{aq}\right]$$

$$\log K_W = \log(10^{-14}) = \log\left[OH^-_{aq}\right] + \log\left[H_3O^+_{aq}\right]$$

$$-14 = \log\left[OH^-_{aq}\right] + \log\left[H_3O^+_{aq}\right]$$

$$14 = -\log\left[OH^-_{aq}\right] + -\log\left[H_3O^+_{aq}\right]$$

$$p[x] \equiv -\log[x]$$

$$14 = pOH + pH$$

pH scale runs from 0 to 14

Which is more Acidic?

Slide 4

acid/base		ave [H⁺]	pH	pOH	ave [OH⁻]
base	blood	5.01×10^{-8}	7.3	6.7	1.99×10^{-7}
	saliva	1×10^{-7}	7		
acid	urine	2.51×10^{-7}			
	cow's milk	3.54×10^{-7}	You do the rest		
	cheese	7.94×10^{-6}			

$$pH \equiv -\log\left[5.01 x 10^{-8}\right] = 7.3$$

is slightly larger than 10^{-8}, so I know it is 7….. something

14-7.3=6.7

$$[OH^-] = 10^{-6.7} = 1.995 x 10^{-7}$$

$$p[x] \equiv -\log[x]$$

$$14 = pH + pOH$$

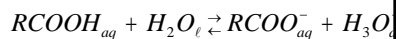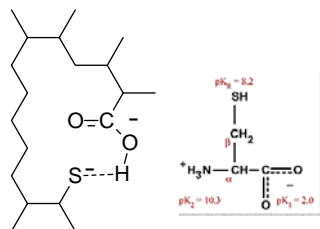$$x = 10^{-pX}$$

Slide 1

What are the two pK$_a$s?

$$px = (-1)(\log x)$$

$$pK_a = (-1)\left(\log\left(6.3 x 10^{-9}\right)\right)$$

$$pK_a = (-1)(-8.2) = 8.2$$

$$RCOOH_{aq} + H_2O_\ell \rightleftarrows RCOO^-_{aq} + H_3O$$

cysteine

What is the K$_a$ of a compound Whose pK$_a$ is 3.7?

$$K_{a,COOH} = 1.0 x 10^{-2}$$

$$K_{a,SH} = 6.3 x 10^{-9}$$

$$x = 10^{-px}$$

$$K_a = 10^{-3.7} = 1.99 x 10^{-4}$$

Slide 2

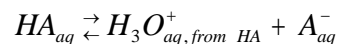"A" students work (without solutions manual)
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Slide 3

Calculating [A-]

This will require an equilibrium calculation

$$HA_{aq} \overset{\rightarrow}{\underset{\leftarrow}{}} H_3O^+_{aq, from\ HA} + A^-_{aq}$$

$$K_a = \frac{\left[A^-_{aq,eq}\right]\left[H_3O^+_{aq,eq}\right]}{\left[HA_{eq,aq}\right]}$$

Slide 4

Generalized Strategy involves comparing K$_a$s

1. Write down ALL possible reactions involving a proton
2. Excluding water, identify all the proton donors as
    1. Strong acid
      a. Strong electrolyte: HNO$_3$, HCl, H$_2$SO$_4$ (No Clean Socks)
      b. Give all strong acid protons to water or alpha dog
      c. Calculate hydronium conc.
      d. Calculate pH
    2. Weak Acid
      a. Identify strongest acid (omega dog, can not hold protons
      b. Has largest K$_a$; smallest charge density anion
      c. Calculate how many protons omega gives up (equil)
      d. Calculate pH
      e. Use to determine what alpha gets
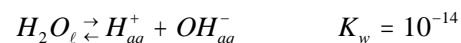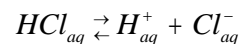
Slide 1

Example Calculations
1.HCl
2.Acetic acid (vinegar)
2.HF
3.B(OH)$_3$ (Boric acid (eye wash))
4.Mixture (HF and phenol)
5.Mixture (H$_2$SO$_4$, HSO$_4^-$)
6.Triethylamine
7.NaAcetate
8.Our heme example

Calculate the pH of 0.004 M HCl

Slide 2

Generalized Strategy involves comparing K$_a$s

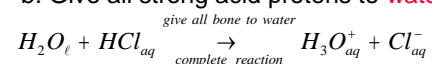1. Write down ALL possible reactions involving a proton

$$HCl_{aq} \rightleftarrows H^+_{aq} + Cl^-_{aq}$$

$$H_2O_\ell \rightleftarrows H^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$

2. Excluding water, identify all the proton donors as
   1. Strong acid
      a. Strong electrolyte: HNO$_3$, HCl, H$_2$SO$_4$ (No Clean Socks)

$$Cl^-_{aq} \; low \; ch\arg e \; density \qquad \text{Omega dog}$$

   b. Give all strong acid protons to water or alpha present

$$H_2O_\ell + HCl_{aq} \xrightarrow[complete \; reaction]{give \; all \; bone \; to \; water} H_3O^+_{aq} + Cl^-_{aq}$$

   c. Calculate hydronium conc. $H_3O^+_{aq} = 0.004\,M$
   d. Calculate pH

Slide 3

$$H_3O^+_{aq} = 0.004\,M$$

Scientific notation allows you to quickly check if
Your answer is in the right "ballpark"

$$pH = -\log\left(4x10^{-3}\right)$$

$$pH = -\log(4) + -\log\left(10^{-3}\right)$$

$$pH = -\log(4) + -(-3)$$

$$pH = -(0.602) + 3 \qquad \text{pH has to be slightly less Than 3}$$

$$pH = 2.39$$

Slide 4

Example Calculations
1.HCl
2.Acetic acid (vinegar)
2.HF
3.B(OH)$_3$ (Boric acid (eye wash))
4.Mixture (HF and phenol)
5.Mixture (H$_2$SO$_4$, HSO$_4^-$)
6.Triethylamine
7.NaAcetate
8.Our heme example

Example: What is the % ionization of commercial vinegar? The label reads 5% acidity (by weight). Vinegar is acetic acid which has the formula $HC_2H_3O_2$. (CH_3COOH) $K_a = 1.8x10^{-5}$
Density of 5% acetic acid 1.0023 g/mL

1. Write down ALL possible reactions involving a proton

$$CH_3COOH_{aq} + H_2O_\ell \rightleftarrows H_3O^+_{aq}, + CH_3COO^-_{aq} \qquad K_a = 1.8x10^{-5}$$

$$H_2O_\ell \rightleftarrows H^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$

2. Excluding water, identify all the proton donors as
   1. Strong acid
      a. Strong electrolyte: HNO_3, HCl, H_2SO_4 (None)
   2. Weak Acid:
   $$CH_3COOH_{aq} + H_2O_\ell \rightleftarrows H_3O^+_{aq}, + CH_3COO^-_{aq} \qquad K_a = 1.8x10^{-5}$$
      a. Calculate how many protons omega gives up (equil)

Example: What is the % ionization of commercial vinegar? The label reads 5% acidity (by weight). Vinegar is acetic acid which has the formula $HC_2H_3O_2$. (CH_3COOH) $K_a = 1.8x10^{-5}$
Density of 5% acetic acid 1.0023g/mL

Know	Don't Know
% by wt.	Need the initial molarity
$K_a = 1.8x10^{-5}$	need the final dissociation

$$\left(\frac{5g_{acetic\ acid}}{100g_{solution}}\right)100g_{solution} = 5g_{acetic\ acid}$$

$$\frac{\left(5g_{acetic\ acid}\right)\left(\frac{1mole_{acetic\ acid}}{2(12)+4(1)+2(16)}\right)}{\left(100g_{solution}\right)\left(\frac{1mL_{solution}}{1.0023g_{solution}}\right)\left(\frac{1L}{10^3mL}\right)} = \frac{\left(5g_{acetic\ acid}\right)\left(\frac{1mole_{acetic\ acid}}{60g_{acetic\ acid}}\right)}{0.0997L} = \frac{0.083mole}{0.0997L} = 0.835M$$

$[HC_2H_3O_2] = 0.8355M$

Why complicate this situation by adding in 10^{-7}
When we get rid off it with an assumption?

Because it creates a habit necessary of multiple rx

	H₂O	**OH⁻**	**H⁺**
	55.5	10^{-7}	10^{-7}

	HC₂H₃O₂	**C₂H₃O₂⁻**	**H⁺**
stoic	1	1	1
conc. init	5%	0	10^{-7}
[**I**nit]	**0.8355**	0	10^{-7}
Change	**-x**	**+x**	**+x**
Assume	**0.8355>>x**	**+x**	10^{-7} << x
[**E**quil]	**0.8355**	**+x**	**+x**

What is the % ionization of commercial vinegar? The label reads 5% acidity (by weight). Density of 5% acetic acid is 1.0023 g/mL. Vinegar is acetic acid which has the formula $HC_2H_3O_2$. (CH_3COOH) $K_a = 1.8x10^{-5}$

$$K_a = \frac{(x)(10^{-7} + x)}{[HA_{init}] - x} \qquad 1.8x10^{-5} = \frac{x^2}{0.8355}$$

	HA	**A**	**H⁺**
Assume	**0.8355>>x**	**+x**	**10-7 << x**

$$0.8355(K_a) = x^2$$

$$\sqrt{0.8355(K_a)} = x$$

$$x = \sqrt{(1.8x10^{-5})(0.8355)} = 0.003878$$

Check: $\boxed{x + 10^{-7} \overset{5\%\ error}{\approx} x?}$

0.0038780
+0.0000001
0.0039779

Sig figs $\left(\frac{0.0000001}{0.0039779}\right)100 = 0.002\%$

$\boxed{0.8355 - x \overset{5\%\ error}{\approx} 0.8355?}$

0.835500
-0.003878
0.831622 $\quad \left(\frac{0.003878}{0.831622}\right)100 = 0.46\%$

Original sig figs were = 0.83
So if we round to 2 sig fig, have Same answer

$$\boxed{pH = (-1)[\log(0.0038778)] = (-1)(-2.41) = 2.41}$$

6

$$\% \, dissociation = 100 \left[\frac{\left[A^-_{eq} \right]}{\left[HA_{aq,initial} \right]} \right]$$

$$\left(\frac{0.003878}{0.835} \right) 100 = 0.46\%$$

What is the % ionization of commercial vinegar? The label reads 5% acidity (by weight). Density of 5% acetic acid is 1.0023 g/mL. Vinegar is acetic acid which has the formula $HC_2H_3O_2$. (CH_3COOH) $K_a = 1.8 \times 10^{-5}$

How does % dissociation or ionization vary with concentration?

[Acetic Acid]	% ionization
1.00 M	0.42%
0.835M	0.46%
0.1 M	1.3%

Observations?

% ionization increases with the lower molarity.

Why should this be so?

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

Dilute by 10 (make less concentrated):

$$Q = \frac{\left(\frac{\left[H^+ \right]}{10} \right)\left(\frac{\left[A^- \right]}{10} \right)}{\frac{\left[HA \right]}{10}} = \frac{\left[H^+ \right]\left[A^- \right]}{\left[HA \right]10} \quad <,=,> \quad K?$$

What does this tell us, if anything?

We have too many reactants, need to shift to the **right**, or dissociate some more.

general rule of thumb: dilution gives more dissociation.

Example Calculations
1. HCl
2. Acetic acid (vinegar)
3. **HF**
4. $B(OH)_3$ (Boric acid (eye wash)) (students Do this one yourself)
5. Mixture (HF and phenol)
6. Mixture (H_2SO_4, HSO_4^-)
7. Triethylamine
8. NaAcetate
9. Our heme example

Panel 1 (top left):

Calculate the F- of a solution of 1.00 M HF.

$K_a = 7.2 \times 10^{-4}$

1. Write down ALL possible reactions involving a proton

$$HF_{aq} \underset{\leftarrow}{\rightarrow} H^+_{aq,F} + F^-_{aq} \qquad K_a = 7.2 \times 10^{-4}$$

$$H_2O_\ell \underset{\leftarrow}{\rightarrow} H^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$

2. Excluding water, identify all the proton donors as
   1. Strong acid
      a. Strong electrolyte: HNO_3, HCl, H_2SO_4 (No Clean Socks)

<div align="center">No Strong Acids (SA)</div>

   2. Weak Acid
      a. Identify strongest acid (omega dog, can not hold protons)
      b. Has largest K_a; smallest charge density anion

$$HF_{aq} \underset{\leftarrow}{\rightarrow} H^+_{aq,F} + F^-_{aq} \qquad K_a = 7.2 \times 10^{-4}$$

      c. Calculate how many protons omega gives up (equil)

Panel 2 (top right):

	H_2O	H^+	OH^-
	55.5	10^{-7}	10^{-7}

	$HF_{(aq)}$	$H^+_{from\ HF}$	F^-
stoic.	1	1	1
Init	1.0	10^{-7}	0
Change	-x	+x	+x
Assum	1>>x	10^{-7}<<x	
Equil	1	x	x

Panel 3 (bottom left):

	$HF_{(aq)}$	$H^+_{from\ HF}$	F^-
Init	1.0	10^{-7}	0
Change	-x	+x	+x
Assum	1>>x	10^{-7}<<x	
Equil	1	x	x

$$K_a = \frac{(x)(x + 10^{-7})}{1-x} \approx \frac{x^2}{1}$$

Check assumptions

$$1(K_a) = x^2$$

$$x = 2.7 \times 10^{-2}$$

$\overset{5\%\ error}{1 - .7x10^{-2} \approx 1?}$
   1.00
   − 0.027
   0.983

$\overset{5\%\ error}{2.7x10^{-2} + 10^{-7} \approx 2.7x10^{-2}\ ?}$
   0.027
   + 0.0000001
   0.0270001

Sig fig is here

Calculate the pH of a solution of 1.00 M HF.
$K_1 = 7.2 \times 10^{-4}$

$0.983 = 1 \qquad 0.0270001 = 0.027$

Panel 4 (bottom right):

	$HF_{(aq)}$	$H^+_{from\ HF}$	F^-
Init	1.0	10^{-7}	0
Change	-x	+x	+x
Assum	1>>x	10^{-7}<<x	
Equil	1	x	x

$$x = 2.7 \times 10^{-2}$$

$$x = [F^-] = 2.7 \times 10^{-2}$$

$$pH = (-1)\left[\log(2.7 \times 10^{-2})\right] = (-1)(-1.568) = 1.6$$

Calculate the F- of a solution of 1.00 M HF.
$K_1 = 7.2 \times 10^{-4}$

Example: Boric acid is commonly used in eyewash solutions to neutralize bases splashed in the eye. It acts as a monoprotic acid, but the dissociation reaction looks different. Calculate the pH of a 0.75 M solution of boric acid, and the concentration of $B(OH)_4^-$.

$$B(OH)_{3,aq} + H_2O_\ell \rightleftarrows B(OH)_{4,aq}^- + H_3O_{aq}^+ \qquad K_a = 5.8x10^{-10}$$

1. Write down ALL possible reactions involving a proton

$$B(OH)_{3,aq} + H_2O_\ell \rightleftarrows B(OH)_{4,aq}^- + H_3O_{aq}^+ \qquad K_a = 5.8x10^{-10}$$

$$H_2O_\ell \rightleftarrows H_{aq}^+ + OH_{aq}^- \qquad K_w = 10^{-14}$$

2. Identify proton donors
   1. strong acids: No Clean Socks?   No SA
   2. Weak acids: $B(OH)_3$

Set up ICAE chart

	H_2O	$\rightleftharpoons$	OH^-	H^+
	55.5		10^{-7}	10^{-7}

	$B(OH)_3$	$+ H_2O \rightleftharpoons$	$B(OH)_4^-$	$+ H^+$
stoic	1	n.a.	1	1
[Init]	0.75		0	10^{-7}
Change	-x		+x	+x
Assume	0.75>>x		x	10^{-7}<<x
Equil	0.75		x	x

$$K_a = \frac{x(x+10^{-7})}{[HA_{init}] - x} \approx \frac{x^2}{[HA_{init}]} \qquad \sqrt{(5.8x10^{-10})0.75} = x = 2.1x10^{-5}$$

$$5.8x10^{-10} = \frac{x^2}{0.75}$$

$B(OH)_3 + H_2O \quad B(OH)_4^- + H^+ \quad K_a = 5.8x10^{-10}$
Calculate the pH of a 0.75 M solution of boric acid.

	$B(OH)_3$	$+ H_2O$	$B(OH)_4^-$	$+ H^+$
[Init]	0.75		0	10^{-7}
Change	-x		+x	+x
Assume	0.75>>x		x	10^{-7}<<x
Equil	0.75		x	x

$$\sqrt{(5.8x10^{-10})0.75} = x = 2.1x10^{-5}$$

$$0.75 - x \overset{5\% \, error}{\approx} 0.75? \qquad x = [B(OH)_4^-] = 2.1x10^{-5}$$

yes

$$x + 10^{-7} \overset{5\% \, error}{\approx} x? \qquad x = [H^+] = 2.1x10^{-5}$$

$$0.000021$$

$$pH = (-1)\log(2.1x10^{-5}) = 4.68 = 4.7$$

$$+\ 0.0000001$$

$$0.0000211$$

$\uparrow$ Sig fig

$B(OH)_3 + H_2O \quad B(OH)_4^- + H^+ \quad K_a = 5.8x10^{-10}$
Calculate the pH of a 0.75 M solution of boric acid.

<u>Example Calculations</u>
1. HCl
2. Acetic acid (vinegar)
3. HF
4. $B(OH)_3$ (Boric acid (eye wash)) (students Do this one yourself)
5. Mixture (HF and phenol)
6. Mixture (H_2SO_4, HSO_4^-)
7. Triethylamine
8. NaAcetate
9. Our heme example

Mixtures of Acids Calculate the pH of a solution that contains 1.0 M HF and 1.0 M HOC_6H_5. Calculate the conc. of $-OC_6H_5$ at this concentration.

1. Write down ALL possible reactions involving a proton

$$HF_{aq} \rightleftarrows H^+_{aq,F} + F^-_{aq} \qquad K_a = 7.2x10^{-4}$$

$$C_6H_5OH_\ell \rightleftarrows H^+_{aq} + C_6H_5O^-_{aq} \qquad K_a = 1.8x10^{-5}$$

$$H_2O_\ell \rightleftarrows H^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$
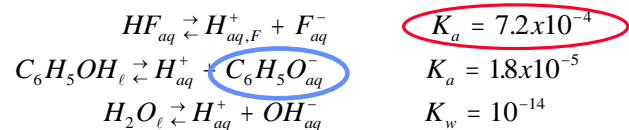
2. Excluding water, identify all the proton donors as
  1. Strong acid   NONE
   2. Weak Acid
   Identify strongest acid (omega dog, can not hold protons)
   Has largest Ka; smallest charge density anion
   Calculate how many protons omega gives up (equil)
   Calculate pH (Use to determine what alpha gets)

HF will control the proton concentration, but
Should include all possible sources to remind ourselves.

H_2O				OH^-	H^+
55.5				10^{-7}	10^{-7}

	HF +	H_2O	$\rightleftarrows$	F^- +	H^+
stoic	1	n.a.		1	1
[Init]	1.0			0	10^{-7}
Change	-x			+x	+x
Assume	1.0>>x			x	10^{-7}<<x
Equil	1.0			x	x

$$K_a = \frac{x(x+10^{-7})}{[HA_{init}]-x} \approx \frac{x^2}{[HA_{init}]} \qquad 7.2x10^{-4} = \frac{x^2}{1}$$

$$\sqrt{(7.2x10^{-4})} = x = 2.7x10^{-2}$$

HF	$H^+ + F^-$	$K_a = 7.2x10^{-4}$
HOC_6H_5	$H^+ + -OC_6H_5$	$K_a = 1.8x10^{-5}$

Calculate the pH of a solution that contains 1.0 M HF and 1.0 M HOC$_6$H$_5$. Calculate the conc. of -OC$_6$H$_5$ at this concentration.

	HF +	H_2O	$\rightleftarrows$	F^- +	H^+
stoic	1	n.a.		1	1
[Init]	1.0			0	10^{-7}
Change	-x			+x	+x
Assume	1.0>>x			x	10^{-7}<<x
Equil	1.0			x	x

$$\sqrt{(7.2x10^{-4})} = x = 2.7x10^{-2}$$

Check assumptions:

$$1 - 2.7x10^{-2} \overset{5\% error}{\approx} 1? \quad \begin{array}{c} 1.0 \\ - 0.027 \\ \hline 0.983 \end{array}$$

Sig fig = 1.0

$$2.7x10^{-2} + 10^{-7} \overset{5\% error}{\approx} 2.7x10^{-2}?$$

$$\begin{array}{c} 0.027 \\ + 0.0000001 \\ \hline 0.0270001 \end{array}$$

Sig fig = 0.027

	HF +	H_2O	$\rightleftarrows$	F^- +	H^+
stoic	1	n.a.		1	1
[Init]	1.0			0	10^{-7}
Change	-x			+x	+x
Assume	1.0>>x			x	10^{-7}<<x
Equil	1.0			x	x
	1.0			$2.7x10^{-2}$	$2.7x10^{-2}$

$$\sqrt{(7.2x10^{-4})} = x = 2.7x10^{-2}$$

$$[H^+] = x = 2.7x10^{-2}$$

Calculate the pH of a solution that contains 1.0 M HF and 1.0 M HOC$_6$H$_5$. Calculate the conc. of -OC$_6$H$_5$ at this concentration.

	HF +	H₂O	⇌	F⁻ +	H⁺

	HF +	H_2O	⇌	F^- +	H^+
stoic	1	n.a.		1	1
[Init]	1.0			0	10^{-7}
Change	-x			+x	+x
Assume	1.0>>x			x	10^{-7}<<x
Equil	1.0			$2.7x10^{-2}$	$2.7x10^{-2}$

	C_6H_5OH+ H_2O		⇌	$C_6H_5O^-$ +	H^+
stoic	1	n.a.		1	1
[Init]	1.0			0	$2.7x10^{-2}$
Change	-x			+x	+x
Assume	1.0>>x			x	x<<$2.7x10^{-2}$
Equil	1.0			x	$2.7x10^{-2}$

	C_6H_5OH+ H_2O		⇌	$C_6H_5O^-$ +	H^+
stoic	1	n.a.		1	1
[Init]	1.0			0	$2.7x10^{-2}$
Change	-x			+x	+x
Assume	1.0>>x			x	x<<$2.7x10^{-2}$
Equil	1.0			x	$2.7x10^{-2}$

$$C_6H_5OH + H_2O_\ell \rightleftharpoons H_3O^+_{aq} + C_6H_5O^-_{aq} \qquad K_a = 1.8x10^{-5}$$

$$K_a = 1.8x10^{-5} = \frac{\left[H_3O^+_{aq,eq}\right]\left[C_6H_5O^-_{aq,eq}\right]}{\left[C_6H_5OH_{eq}\right]}$$

$$\left[2.7x10^{-2}\right] + x \overset{5\% error}{\approx} \left[2.7x10^{-2}\right]?$$

$$100\left(\frac{6.66x10^{-4}}{2.7x10^{-2}}\right) = 2.46\%$$

$$K_a = 1.8x10^{-5} = \frac{(2.7x10^{-2}+x)x}{1-x} \approx \frac{(2.7x10^{-2})x}{x} \approx 2.7x10^{-2}$$

$$x = \left[C_6H_5O^-_{aq,eq}\right] = 6.66x10^{-4}$$

$$x = \frac{1.8x10^{-5}}{\left[2.7x10^{-2}\right]} = 6.66x10^{-4}$$

Calculate the pH of a solution that contains 1.0 M HF and 1.0 M HOC₆H₅. Calculate the conc. of ⁻OC₆H₅ at this concentration.

Example Calculations
1. HCl
2. Acetic acid (vinegar)
3. HF
4. B(OH)₃ (Boric acid (eye wash)) (students Do this one yourself)
5. Mixture (HF and phenol)
6. **Mixture (H₂SO₄, HSO₄⁻)**
7. Triethylamine
8. NaAcetate
9. Our heme example

Example: calculate the pH of 0.0010 M sulfuric acid

1. Write down ALL possible reactions involving a proton

$$H_2SO_{4,aq} + H_2O \overset{\rightarrow}{\underset{\leftarrow}{}} HSO^-_{4aq,F} + H_3O^+_{aq} \qquad K_a = l\arg e$$

$$HSO^-_{4,aq} + H_2O_\ell \overset{\rightarrow}{\underset{\leftarrow}{}} H_3O^+_{aq} + SO^{2-}_{4.aq} \qquad K_a = 1.2x10^{-2}$$

$$H_2O_\ell \overset{\rightarrow}{\underset{\leftarrow}{}} H^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$

2. Excluding water, identify all the proton donors as
   1. Strong acid
      a. Strong electrolyte: HNO₃, HCl, H₂SO₄ (No Clean Socks)

$$H_2SO_{4,aq} + H_2O \overset{\rightarrow}{\underset{\leftarrow}{}} HSO^-_{4aq,F} + H_3O^+_{aq} \qquad K_a = l\arg e$$

      b. Give all strong acid protons to water or alpha dog

Panel 1 (top left)

1	Pure Water	H_2O	OH^-	H^+	
		55.5	10^{-7}	10^{-7}	

2	Control/complete	H_2SO_4	HSO_4^-	H^+	
	stoic.	1	1	1	
	[init]	.0010	0	10^{-7}	
	complete	0	0.0010	$0.0010+10^{-7}$	
		0	0.0010	0.0010	

3	stoic.		HSO_4^-	H^+	SO_4^{2-}
			1	1	1
	[Init]		0.0010	0. 0010	0
	Change		-x	+x	+x
	Assume?		0.0010>x	0.0010>x	+x
	[Equil]		0.0010	0.0010	x

$$K_{a2} = \frac{\left[H_3O^+_{aq,eq}\right]\left[SO^{2-}_{4,aq,eq}\right]}{\left[HSO^-_{4,aq,eq}\right]}$$

$$K_{a2} = 1.2x10^{-2} = \frac{[0.001+x][x]}{[0.001]-x} \overset{5\% \, error}{\approx} \frac{0.001x}{0.001} = x$$

$$K_{a2} = 1.2x10^{-2} = x = \left[SO^{2-}_{4,aq}\right]$$

$$1.2x10^{-2} + 0.001 \overset{5\% \, error}{\approx} 0.001? \quad \boxed{NO!}$$

Example: calculate the pH of 0.0010 M sulfuric acid; $K_{a2} = 1.2x10^{-2}$

Panel 2 (top right)

$$1.2x10^{-2} + 0.001 \overset{5\% \, error}{\approx} 0.001? \qquad \left(\frac{1.2x10^{-2}}{0.001}\right)100 = 1200\% \, error!$$

Here is our first example in which we can not make assumptions

stoic.	HSO_4^-	H^+	SO_4^{2-}
	1	1	1
[Init]	0.0010	0. 0010	0
Change	-x	+x	+x
~~Assume?~~	~~0.001>x~~	~~0.001>x~~	~~+x~~
[Equil]	0.001-x	0.001+x	x

$$K_{a2} = 1.2x10^{-2} = \frac{[0.001+x][x]}{[0.001-x]}$$

$$(1.2x10^{-2})(0.001-x) = (0.001+x)x$$

$$1.2x10^{-5} - 1.2x10^{-2}x = 0.001x + x^2$$

$$x^2 + 0.001x + 1.2x10^{-2}x - 1.2x10^{-5} = 0$$

$$x^2 + 0.013x - 1.2x10^{-5} = 0$$

Example: calculate the pH of 0.0010 M sulfuric acid; $K_{a2} = 1.2x10^{-2}$

Panel 3 (bottom left)

$$x^2 + 0.013x - 1.2x10^{-5} = 0$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-0.013 \pm \sqrt{(0.013)^2 - 4(1)(-0.000012)}}{2(1)}$$

$$x = \frac{-0.013 \pm \sqrt{2.17x10^{-4}}}{2}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

-Solution gives a neg Number which is not allowed

$$x = \frac{-0.013 \pm 0.0147}{2}$$

$$x = 8.65x10^{-4}$$

$[SO_4^{2-}]=x$

[H$^+$]=0.001
+0.000865
0.001865

pH=-log(0.001865)=2.73

Panel 4 (bottom right)

Successive Approximations
(iterations)

Alternative Strategy to
going to "exact equil. Expression"

ITERATIVE SOLUTIONS

Why? – because the real body or real world
Is much too complex to always be able to
Find an exact equilibrium expression

Calculate proton concentration of 0.100 M HNO_2 using the **iterative method** ($K_a=6.0\times10^{-4}$)

		H_2O	OH^-	H^+
1	**Pure Water**	**55.5**	**10^{-7}**	**10^{-7}**
		HNO_2	NO_2	H^+
	stoic.	1	1	1
2	**[I**nit]	**0.100**	0	**10^{-7}**
	Change	**-x**	**+x**	**+x**
	Assume	**0.100>>x**	**x**	**x>>10^{-7}**
	[Equil]	**0.100**	**x**	**x**
	Calc 1			7.7×10^{-3}
3	**New Equil**	**0.100-7.7x10⁻³**	**x''**	**x''**
	Calc 2			7.44×10^{-3}
4	**New New Equil**	**0.100-7.44x10⁻³**	**x'''**	**x'''**
	Calc 3			7.45×10^{-3}

$$K_a = \frac{x^2}{[HA_{eq}]} \qquad \sqrt{K_a[HA_{eq}]} = x$$

$$x'' = \sqrt{(6.0x10^{-4})(0.1-7.7x10^{-3})} = \sqrt{(6.0x10^{-4})(0.0923)}$$

$$x = \sqrt{(6.0x10^{-4})(0.1)} = 7.7x10^{-3} \qquad x'' = \sqrt{5.538x10^{-5}} = 7.44x10^{-3}$$

Converging, plausible answer for iterative method: 0.100 M HNO_2, $K_a=6.0\times10^{-4}$
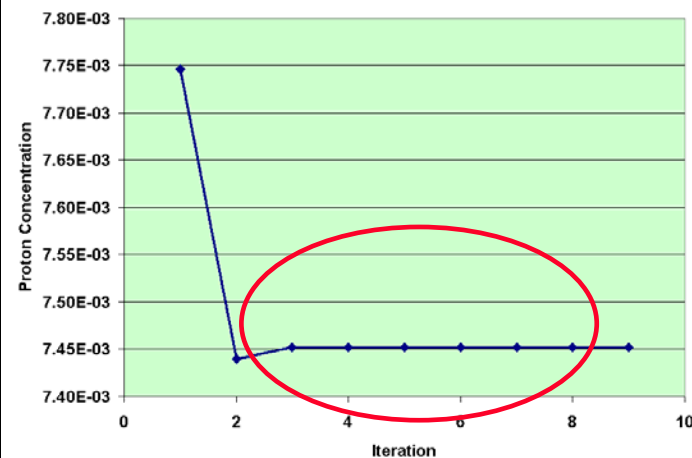
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Module #17B:
Acid Base Ionization Computations
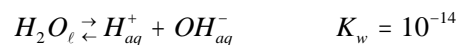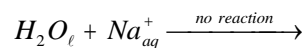
Weak Bases

I WANT YOU TO PRACTICE EVERY DAY!

Example Calculations
1. HCl
2. Acetic acid (vinegar)
3. HF
4. $B(OH)_3$ (Boric acid (eye wash)) (students Do this one yourself)
5. Mixture (HF and phenol)
6. Mixture (H_2SO_4, HSO_4^-)
7. **Triethylamine**
8. NaAcetate
9. Our heme example

Calculation with Weak Base

Calc. the [OH], [H], and pH of 0.20 M solns of triethyl**amine**, $K_b = 4.0\times10^{-4}$

		H_2O	H^+	$OH-$
1		55.5	10^{-7}	10^{-7}
	B	H_2O	BH^+	$OH-$
stoic	1	1	1	1
2 [**I**nit]	0.20		0	10^{-7}
Change	-x		+x	+x
Assum	0.20>>x		x	$10^{-7} < x$
Equil	0.20		x	x

Calc. the [OH], [H], and pH of 0.20 M solns of triethylamine, $K_b = 4.0\times10^{-4}$

		H_2O	H^+	$OH-$
1		55.5	10^{-7}	10^{-7}
	B	H_2O	BH^+	$OH-$
stoic	1	1	1	1
2 [**I**nit]	0.20		0	10^{-7}
Change	-x		+x	+x
Assum	0.20>>x		x	$10^{-7} < x$
Equil	0.20		x	x

$$K_b = 4.0x10^{-4} = \frac{x(x+10^{-7})}{0.2-x} \approx \frac{x^2}{0.2}$$

$$\sqrt{(4.0x10^{-4})0.2} = x = 8.94x10^{-3}$$

$$8.94x10^{-3} + 10^{-7} \overset{5\% \, error}{\approx} 8.94x10^{-3} \,?$$

$$0.20 - 8.94x10^{-3} \overset{5\% \, error}{\approx} 0.2 \,?$$

```
  0.00894           0.20
+ 0.00000001      - 0.00894
  0.00895001        0.19106

Rounds to 0.0089   Rounds to 0.20
```

$$x = \left[OH^-\right] = 8.94x10^{-3}$$
$$pOH = (-1)\left[\log(0.00894)\right] = 2.048$$
$$pH = 14 - 2.048 = 11.95$$

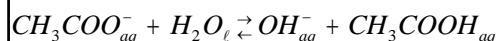Calc. the [OH], [H], and pH of 0.20 M solns of triethylamine, $K_b = 4.0\times10^{-4}$

Example Calculations
1. HCl
2. Acetic acid (vinegar)
3. HF
4. $B(OH)_3$ (Boric acid (eye wash)) (students Do this one yourself)
5. Mixture (HF and phenol)
6. Mixture (H_2SO_4, HSO_4^-)
7. Triethylamine
8. NaAcetate
9. Our heme example

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Panel 1 (top-left)

Write all reactions involving protons, hydroxides

$$Na(CH_3COO) + H_2O_\ell \rightleftarrows Na^+_{aq} + CH_3COO^-_{aq}$$

$$CH_3COO^-_{aq} + H_2O_\ell \rightleftarrows OH^-_{aq} + CH_3COOH_{aq}$$

$$H_2O_\ell + Na^+_{aq} \xrightarrow{\text{no reaction}}$$

$$H_2O_\ell \rightleftarrows H^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$
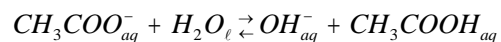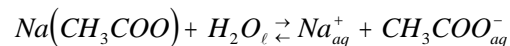
Determine who is omega and will donate

$$CH_3COO^-_{aq} + H_2O_\ell \rightleftarrows OH^-_{aq} + CH_3COOH_{aq}$$

Hmm, a slight problem – we don't know K_b

If we place Na acetate in solution (to make a 0.1 M solution) what are the main species present? What will be the pH of the solution? $K_a = 1.8 \times 10^{-5}$

Panel 2 (top-right)

$$CH_3COOH_{aq} + H_2O_\ell \rightleftarrows CH_3COO^-_{aq} + H_3O^+_{aq} \qquad K_a = 1.8 \times 10^{-5}$$

$$CH_3COO^-_{aq} + H_3O^+_{aq} \rightleftarrows CH_3COOH_{aq} + H_2O_\ell \qquad \frac{1}{K_a}$$

$$H_2O_\ell + H_2O_\ell \rightleftarrows H_3O^+_{aq} + OH^-_{aq} \qquad K_w = 10^{-14}$$

$$CH_3COO^-_{aq} + H_2O_\ell \rightleftarrows CH_3COOH_{aq} + OH^-_{aq} \qquad K_b = \frac{1}{K_a} K_w$$
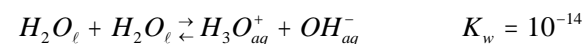
$$\boxed{K_w = K_a K_b}$$

$$\frac{10^{-14}}{1.8 \times 10^{-5}} = K_b = 5.55 \times 10^{-10}$$

If we place Na acetate in solution (to make a 0.1 M solution) what are the main species present? What will be the pH of the solution? $K_a = 1.8 \times 10^{-5}$

Panel 3 (bottom-left)

$K_b = 5.55 \times 10^{-10}$

1

	H₂O	H⁺	OH⁻
	55.5	10^{-7}	10^{-7}

$$CH_3COO^- + H_2O = CH_3COOH + OH^-$$

2

	CH₃COO⁻	CH₃COOH	OH⁻
stoich	1	1	1
[Init]	0.1	0	10^{-7}
Change	-x	+x	10^{-7} +x
Sum	0.1-x	0+x	10^{-7} +x
Assume	x<<<0.1		x>>>10^{-7}
[Equil]	0.1	x	x

If we place Na acetate in solution (to make a 0.1 M solution) what are the main species present? What will be the pH of the solution? $K_a = 1.8 \times 10^{-5}$

Panel 4 (bottom-right)

$K_b = 5.55 \times 10^{-10}$

$$CH_3COO^- + H_2O = CH_3COOH + OH^-$$

	CH₃COO⁻	CH₃COOH	OH⁻
stoich	1	1	1
[Init]	0.1	0	10^{-7}
Change	-x	+x	10^{-7} +x
Sum	0.1-x	0+x	10^{-7} +x
Assume	x<<<0.1		x>>>10^{-7}
[Equil]	0.1	x	x

$$5.55 \times 10^{-10} = \frac{[OH^-_{aq,eq}][CH_3COOH_{aq},eq]}{[CH_3COO^-_{aq,eq}]} = \frac{(x + 10^{-7})x}{0.1 - x} \approx \frac{x^2}{0.1}$$

$$7.45 \times 10^{-6} + 10^{-7} \overset{5\% \, error}{\approx} 7.45 \times 10^{-6}?$$

$$5.55 \times 10^{-10} = \frac{x^2}{0.1} \qquad 0.1 - 7.45 \times 10^{-6} \overset{5\% \, error}{\approx} 0.1? \qquad \text{No}$$

$$\sqrt{(5.55 \times 10^{-10})0.1} = x \qquad \text{yes}$$

$$x = 7.45 \times 10^{-6}$$

If we place Na acetate in solution (to make a 0.1 M solution) what are the main species present? What will be the pH of the solution? $K_a = 1.8 \times 10^{-5}$

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	$CH_3COO^- + H_2O = CH_3COOH + OH^-$		
stoich	1	1	1
[Init]	0.1	0	10^{-7}
Change	-x	+x	10^{-7} +x
Sum	0.1-x	0+x	10^{-7} +x
Assume	x<<<0.1		x>>>10^{-7}
[Equil]	0.1	x	x
Equil new	0.1-x	x	x+10^{-7}

$$K_b = 5.55x10^{-10} = \frac{[x][x+10^{-7}]}{[0.1-x]}$$

$$(5.55x10^{-10})[0.1-x] = [x][x+10^{-7}] = x^2 + (10^{-7})x$$

If we place Na acetate in solution (to make a 0.1 M solution) what are the main species present? What will be the pH of the solution? $K_a = 1.8x10^{-5}$

$$(5.55x10^{-10})[0.1-x] = [x][x+10^{-7}] = x^2 + (10^{-7})x$$

$$5.55x10^{-11} - (5.55x10^{-10})x = x + (10^{-7})x$$

$$x^2 + (10^{-7})x + (5.55x10^{-10})x - 5.55x10^{-11} = 0$$

$$x^2 + (1.00555x10^{-7})x - 5.55x10^{-11} = 0$$

$$x = \frac{-1.00555x10^{-7} \pm \sqrt{(1.00555x10^{-7})^2 - 4(1)(-5.55x10^{-11})}}{2(1)}$$

$$ax^2 + bx + c = 0$$

$$x = \frac{-1.00555x10^{-7} \pm \sqrt{1.01103x10^{-14} + 2.22x10^{-10}}}{2}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-1.00555x10^{-7} \pm \sqrt{2.22x10^{10}}}{2}$$

$$x = \frac{-1.00555x10^{-7} \pm 1.49x10^{-5}}{2} = 7.399x10^{-6}$$

Before we got 7.45x10^{-6}

"A" students work (without solutions manual) ~ 10 problems/night.
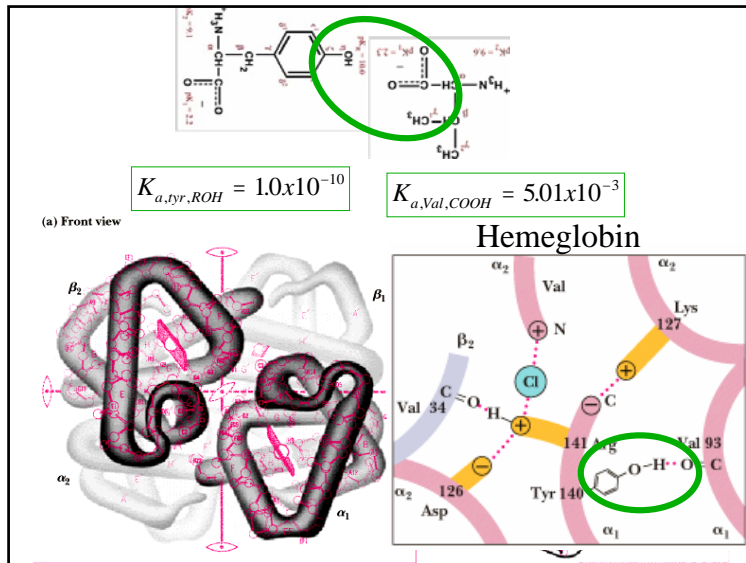
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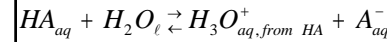508-3119
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Module #17B:
Acid Base Ionization Computations

Biological Chemistry

Example Calculations
1. HCl
2. Acetic acid (vinegar)
3. HF
4. $B(OH)_3$ (Boric acid (eye wash)) (students Do this one yourself)
5. Mixture (HF and phenol)
6. Mixture (H_2SO_4, HSO_4^-)
7. Triethylamine
8. NaAcetate
9. Our heme example

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Slide 1:

$K_{a,tyr,ROH} = 1.0x10^{-10}$

$K_{a,Val,COOH} = 5.01x10^{-3}$

(a) Front view

Hemeglobin

Slide 2:

Which pH (2, 7, 11) is most favorable for the formation of a hydrogen bond between Val and tyr in hemoglobin assuming that we define favorable as having the most possible H bonds.

$K_{a,Val,COOH} = 5.01x10^{-3}$

$K_{a,tyr,ROH} = 1.0x10^{-10}$

$$HA_{aq} + H_2O_\ell \underset{\leftarrow}{\overset{\rightarrow}{}} H_3O^+_{aq,from\ HA} + A^-_{aq}$$

$$\%dissociated = 100\frac{[A^-_{aq,eq}]}{[HA_{init}]}$$

$$K_a = \frac{[A^-_{aq,eq}][H_3O^+_{aq,eq}]}{[HA_{eq,aq}]}$$

Mass balance

$$\frac{[A^-_{aq,eq}][H_3O^+_{aq,eq}]}{K_a} = [HA_{eq,aq}]$$

$$[HA_{init}] = [HA_{eq,aq}] + [A^-_{aq,eq}]$$

$$\%dissociated = \frac{100[A^-_{aq,eq}]}{[HA_{eqt}] + [A^-_{aq,eq}]}$$

$$\%dissociated = \frac{100[A^-_{aq,eq}]}{\frac{[A^-_{aq,eq}][H_3O^+_{aq,eq}]}{K_a} + [A^-_{aq,eq}]}$$

Slide 3:

Which pH (2, 4.7, 7, 11) is most favorable for the formation of a hydrogen bond between Val and tyr in hemoglobin assuming that we define favorable has having the most possible H bonds

$K_{a,Val,COOH} = 5.01x10^{-3}$

$K_{a,tyr,ROH} = 1.0x10^{-10}$

$$\%dissociated = \frac{100[A^-_{aq,eq}]}{\frac{[A^-_{aq,eq}][H_3O^+_{aq,eq}]}{K_a} + [A^-_{aq,eq}]}$$

$$\%dissociated = \frac{100}{\frac{[H_3O^+_{aq,eq}]}{K_a} + 1}$$

$pH2; [H^+] = 10^{-2}$

$$\%dissociatedCOOH = \left[\frac{100}{\frac{[10^{-2}]}{5.01x10^{-3}} + 1}\right] = 33.33$$

pH	10^(-pH) [H+]	valanine Ka COOH 5.00E-03 %ionized	tyrosine Ka OH 1.00E-10 %ionized
2	0.01	33.33333	1.00E-06
4.7	1.99526E-05	99.60253	5.01E-04
7	0.0000001	99.998	9.99E-02
10	1E-10	100	5.00E+01

Repeat procedure
With tyrosine

Slide 4:

$K_{a,tyr,ROH} = 1.0x10^{-10}$

$K_{a,Val,COOH} = 5.01x10^{-3}$

pH	10^(-pH) [H+]	valanine Ka COOH 5.00E-03 %ionized	tyrosine Ka OH 1.00E-10 %ionized
2	0.01	33.33333	1.00E-06
4.7	1.99526E-05	99.60253	5.01E-04
7	0.0000001	99.998	9.99E-02
10	1E-10	100	5.00E+01

Which pH is best?

Hint: Want Val ionized
Tyr not ionized

Slide 1 (top-left)

"A" students work
(without solutions manual)
~ 10 problems/night.

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Module #17B:
Acid Base Ionization
Computations

When should we
Be making assumptions?

Slide 2 (top-right)

Example on Using Simplifications   Module 17A

If 1.0 mol NOCl is placed in a 2.0 L flask what are the equilibrium concentrations of NO and Cl_2 given that at 35 ℃ the equilibrium constant, K_c, is 1.6×10^{-5} mol/L?

Red herrings: 35 ℃ is a red herring

Clues?
   K is "small" compared to others (<<< 1) we have worked with !!!!!

Example 2 $CO_{2,g} + H_{2,g} \rightleftarrows CO_g + H_2O_g$ K_c is 0.64.

EXAMPLE 3: $N_2O_4 \rightleftarrows 2NO_{2(g)}$ $K_c = 0.36M$ **We will define Small in the Next chapter!**

Example 4: $H_{2,g} + I_{2,g} \rightleftarrows 2HI_{(g)}$ K_p is 1×10^{-2}.

Slide 3 (bottom-left)

We want to know when assumptions are valid.

	$HA_{(aq)}$	$H^+_{from\ HA}$	A^-
Init	HA_{INIT}	10^{-7}	0
Change	$-x$	$+x$	$+x$
Equil	$HA_{INIT}-x$	$10^{-7}+x$	x

$$K_a = \frac{(x)(x+10^{-7})}{[HA_{INIT}]-x} \approx \frac{x^2}{[HA_{INIT}]}$$

$$\left(\frac{x}{[HA_{init}]}\right)100 < 5\% \ ???$$

%ionized

Slide 4 (bottom-right)

The issue is small Ka with respect
To the initial concentration!!

Considering a simple system

$$HA_{eq} \rightleftarrows A^-_{eq} + H^-_{eq}$$

Mass balance

$$[HA_{init}] = [HA_{eq,aq}] + [A^-_{aq,eq}]$$

$$\% dissociated = \left(\frac{[A^-_{aq,eq}]}{[HA_{eq}]+[A^-_{aq,eq}]}\right)100$$

$$K_a = \frac{[A^-_{aq,eq}][H_3O^+_{aq,eq}]}{[HA_{eq,aq}]}$$

$$[A^-_{aq,eq}][H_3O^+_{aq,eq}] = [HA_{eq,aq}]K_a$$

$$[A^-_{aq,eq}]^2 = [HA_{eq,aq}]K_a$$

$$[A^-_{aq,eq}] = \sqrt{[HA_{eq,aq}]K_a}$$

$$\% dissociated = \left(\frac{\sqrt{K_a[HA_{eq}]}}{[HA_{eq}]+\sqrt{K_a[HA_{eq}]}}\right)100$$

OK this is not a nice equation
Do you need to know it?

% Ionization

2.50E+01
2.00E+01
1.50E+01
1.00E+01
5.00E+00
0.00E+00

Error too large

Error OK

0   0.1   0.2   0.3   0.4   0.5   0.6   0.7   0.8

Safe to make assumption   iffy   **Conc.**   Never make assumption

$K_A = 10^{-7}$ 5×10^{-6} 5×10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1}
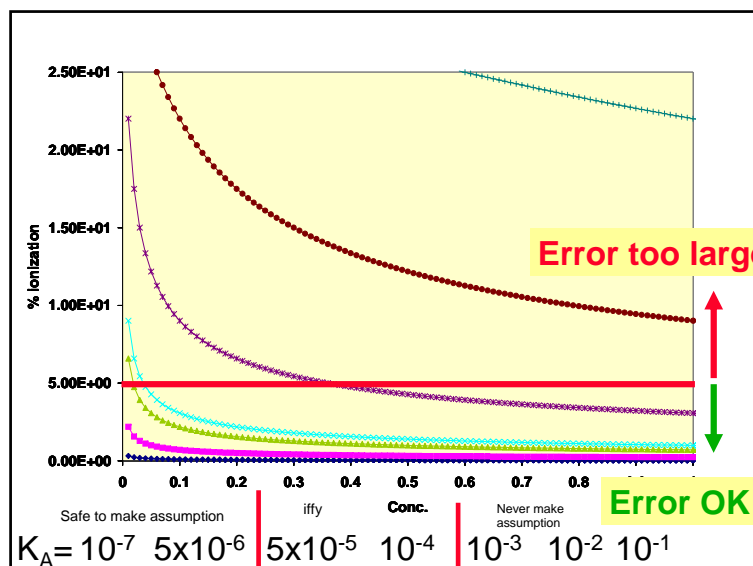
Rule of Thumb

Small K ~ $< 10^{-6}$

Sort of small $10^{-6} < K < 10^{-4}$

Large K ~ $> 10^{-3}$

I WANT YOU TO PRACTICE EVERY DAY!

"A" students work
(without solutions manual)
~ 10 problems/night.

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**Module #17B:
Acid Base Ionization
Computations**

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