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

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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?

http://www.jenner.ac.uk/PPD/ Ionization constants for proteins

$$\text{RCOOH}_{aq} + H_2O_{aq} \rightarrow \text{RCOO}^{-}_{aq} + H_3O^+_{aq}$$

$$\text{RSH}_{aq} + H_2O_{aq} \rightarrow \text{RS}^-_{aq} + H_3O^+_{aq}$$

$R$ refers to rest of protein

Control of protein shape is due to fraction of sites charged
Protein folding due to FRACTION of sites charged

\[ K_{a,Val, NH_2} = 2.5 \times 10^{-4} \]

\[ K_{a,Fal, COOH} = 5.01 \times 10^{-3} \]

\[ K_{a,pY, ROH} = 1.0 \times 10^{-10} \]

Hemoglobin

% Ionized (dissociated)

\[ HA_{aq} \rightleftharpoons H_3O^+_{aq}, \text{from } HA + A^-_{aq} \]

\[ \%\text{dissociation} = 100 \frac{\text{amount dissociated (M)}}{\text{initial concentration (M)}} \]

\[ \%\text{dissociation} = 100 \frac{[A^-]}{[HA_{aq,initial}]} \]

This seems pretty straightforward

Calculating [A-]

This will require knowing \([H_3O_{aq}^+]\)

\[ HA_{aq} \rightleftharpoons H_3O^+_{aq,从} HA + A^-_{aq} \]

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

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

\( K_a \) and \( K_b \) tell us about the possibility of donating protons, not what the solution Acidity is

Define another comparison number: pH

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Module #17B: Acid Base Ionization Computations

pH, pOH, pKa
Chemists are **Lazy**

To shorten calculations use log:

\[
\log(ab) = \log(a) + \log(b)
\]

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

\[
\log(a)^x = x \log(a)
\]

\[
\log\left(\frac{1}{a^x}\right) = -x \log(a)
\]

\[
K_w = 10^{-14} = [\text{OH}^-_{aq}][\text{H}_3\text{O}^+_{aq}]
\]

\[
\log K_w = \log(10^{-14}) = \log[\text{OH}^-_{aq}] + \log[\text{H}_3\text{O}^+_{aq}]
\]

\[
-14 = \log[\text{OH}^-_{aq}] + \log[\text{H}_3\text{O}^+_{aq}]
\]

\[
14 = -\log[\text{OH}^-_{aq}] + \log[\text{H}_3\text{O}^+_{aq}]
\]

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

\[
14 = pOH + pH
\]

pH scale runs from 0 to 14

Which is more Acidic?

\[
K = \frac{[\text{OH}^-_{eq}][\text{H}_3\text{O}^+_{eq}]}{[\text{H}_2\text{O}]}^2
\]

Assumption that 55.5 molar is relative unchanged

\[
K[H_2O]^2 = [\text{OH}^-_{eq}][\text{H}_3\text{O}^+_{eq}]
\]

\[
K[55.5]^2 = [\text{OH}^-_{eq}][\text{H}_3\text{O}^+_{eq}]
\]

\[
K[55.5]^2 = K_w = 10^{-14}
\]

\[
K_w = 10^{-14} = [\text{OH}^-_{eq}][\text{H}_3\text{O}^+_{eq}]
\]

<table>
<thead>
<tr>
<th>acid/base</th>
<th>ave [H⁺]</th>
<th>pH</th>
<th>pOH</th>
<th>ave [OH⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>base</td>
<td>blood 5.01x10⁻⁸</td>
<td>7.3</td>
<td>6.7</td>
<td>1.99x10⁻⁷</td>
</tr>
<tr>
<td>saliva</td>
<td>1x10⁻⁷</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid</td>
<td>urine 2.51x10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cow’s milk</td>
<td>3.54x10⁻⁷</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cheese</td>
<td>7.94x10⁻⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

You do the rest

\[
pH \equiv -\log[5.01x10^{-8}] = 7.3
\]

\[
# is slightly larger than 10⁻⁶, so I know it is 7..... something
\]

14-7.3=6.7

\[
[\text{OH}^-] = 10^{-6.7} = 1.995x10^{-7}
\]
What are the two pK$_a$s?

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

$$ pK_a = (-1)(\log(6.3 \times 10^{-9})) $$

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

RCOOH$_{aq} \rightleftharpoons H_2O^+ + RCOO^{-} $$

What is the $K_a$ of a compound whose pK$_a$ is 3.7?

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

$$ K_a = 10^{-3.7} = 1.99 \times 10^{-4} $$

Calculating [A-]

This will require an equilibrium calculation

$$ HA_{aq} \rightleftharpoons H_3O^+_{aq, from HA} + A^{-}_{aq} $$

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

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

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~ 10 problems/night.

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Module #17B:
Acid Base Ionization
Computations
Example Calculations

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

Calculate the pH of 0.004 M HCl

\[
H_3O^+_{aq} = 0.004 \text{ M}
\]

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

\[
pH = - \log(4 \times 10^{-3})
\]

\[
pH = - \log(4) + - \log(10^{-3})
\]

\[
pH = - \log(4) + -( -3)
\]

\[
pH = -(0.602) + 3 \quad \text{pH has to be slightly less Than 3}
\]

\[
pH = 2.39
\]

Generalized Strategy involves comparing \( K_a \)s

1. Write down **ALL** possible reactions involving a proton

\[
\begin{align*}
\text{HCl}_{aq} & \leftrightarrow \text{H}^+_{aq} + \text{Cl}^-_{aq} \\
\text{H}_2\text{O}_{aq} & \leftrightarrow \text{H}^+_{aq} + \text{OH}^-_{aq} \\
\text{K}_w & = 10^{-14}
\end{align*}
\]

2. Excluding water, identify all the proton donors as

   a. Strong acid
      
      i. Strong electrolyte: HNO₃, HCl, H₂SO₄ (No Clean Socks)
      
      \( \text{Cl}^-_{aq} \, \text{low charge density} \, \text{Omega dog} \)

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

   \[
   \text{H}_2\text{O}_{aq} + \text{HCl}_{aq} \quad \text{complete reaction} \quad \text{H}_3\text{O}^+_{aq} + \text{Cl}^-_{aq}
   \]

   c. Calculate hydronium conc. \( \text{H}_3\text{O}^+_{aq} = 0.004 \text{ M} \)

   d. Calculate pH

Example Calculations

1. **HCl**
2. **Acetic acid (vinegar)**
3. HF
4. B(OH)₃ (Boric acid (eye wash))
5. Mixture (HF and phenol)
6. Mixture (H₂SO₄, HSO₄⁻)
7. Triethylamine
8. NaAcetate
9. 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 \( \text{HC}_2\text{H}_3\text{O}_2 \). \( K_a = 1.8 \times 10^{-5} \)

Density of 5% acetic acid is 1.0023 g/mL

1. Write down **ALL** possible reactions involving a proton

   \[
   \text{CH}_3\text{COOH}_{\text{aq}}^{-} + \text{H}_2\text{O}_{\text{aq}} \rightarrow \text{H}_2\text{O}_{\text{aq}}^+ + \text{CH}_3\text{COO}^-_{\text{aq}}
   \]

   \[
   K_w = 10^{-14}
   \]

2. Excluding water, identify all the proton donors as:

   a. Strong acid
   - Strong electrolyte: HNO₃, HCl, H₂SO₄ (None)
   b. Weak Acid:
   - Solution acetic acid
     - Strong electrolyte: HNO₃, HCl, H₂SO₄ (None)

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

   \[
   \left[ \text{HC}_2\text{H}_3\text{O}_2 \right] = 0.8355 M
   \]

   Why complicate this situation by adding in 10⁻⁷

   When we get rid of it with an assumption?

   Because it creates a habit necessary of multiple rx

   \[
   \begin{align*}
   \text{H}_2\text{O} & \quad \text{OH}^- \quad \text{H}^+ \\
   \text{55.5} & \quad 10^{-7} \quad 10^{-7}
   \end{align*}
   \]

   \[
   \begin{align*}
   \text{HC}_2\text{H}_3\text{O}_2 & \quad \text{C}_2\text{H}_3\text{O}_2^- \quad \text{H}^+ \\
   \text{stoic} & \quad 1 \quad 1 \quad 1 \\
   \text{conc. init} & \quad 5\% \quad 0 \quad 10^{-7} \\
   \text{[Init]} & \quad \text{0.8355} \quad 0 \quad 10^{-7} \\
   \text{Change} & \quad -x \quad +x \quad +x \\
   \text{Assume} & \quad \text{0.8355} \gg x \quad +x \quad 10^{-7} \ll x \\
   \text{[Equil]} & \quad \text{0.8355} \quad +x \quad +x
   \end{align*}
   \]

   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 \( \text{HC}_2\text{H}_3\text{O}_2 \). \( K_a = 1.8 \times 10^{-5} \)

   \[
   K_a = \frac{(x)(10^{-7} + x)}{[\text{HA}_{\text{aq}}]} = 1.8 \times 10^{-5} = \frac{x^2}{0.8355}
   \]

   \[
   x = \sqrt{(1.8 \times 10^{-5})(0.8355)} = 0.003878
   \]

   Original sig figs were = 0.83

   So if we round to 2 sig fig, have

   Same answer

   \[
   \sqrt{0.831622} = 0.831622 \times \frac{100}{100} = 0.46
   \]

\[\text{pH} = (-1)[\log(0.003878)] = (-1)(-2.41) = 2.41\]

\[\text{Sig figs: 0.0039779} \times \frac{100}{100} = 0.0024\%\]
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\(\text{H}_2\text{O}_2\). (CH\(_3\)COOH) \(K_a = 1.8 \times 10^{-5}\)

\[
\%\text{dissociation} = 100 \left( \frac{[A^-]}{[HA_{\text{initial}}]} \right)
\]

\[
\left( \frac{0.003878}{0.835} \right) \times 100 = 0.46\%
\]

How does % dissociation or ionization vary with concentration?

<table>
<thead>
<tr>
<th>[Acetic Acid]</th>
<th>% ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 M</td>
<td>0.42%</td>
</tr>
<tr>
<td>0.835 M</td>
<td>0.46%</td>
</tr>
<tr>
<td>0.1 M</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

Observations?

% ionization increases with the lower molarity.

Why should this be so?

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

Dilute by 10 (make less concentrated):

\[
Q = \frac{[H^+] [A^-]}{10} = \frac{[H^+] [A^-]}{[HA]} <, =, > K?
\]

What does this tell us, if anything?

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

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\(_2\)SO\(_4\), HSO\(_4^-\))
7. Triethylamine
8. NaAcetate
9. Our heme example
1. Write down ALL possible reactions involving a proton

\[ HF_{aq} \rightarrow H^+_{aq,F} + F^-_{aq} \quad K_a = 7.2 \times 10^{-4} \]

\[ H_2O \rightarrow H^+_{aq} + OH^-_{aq} \quad K_w = 10^{-14} \]

2. Excluding water, identify all the proton donors as

1. Strong acid
   a. Strong electrolyte: HNO₃, HCl, H₂SO₄ (No Clean Socks)
   No Strong Acids (SA)

2. Weak Acid
   a. Identify strongest acid (omega dog, can not hold protons)
   b. Has largest \( K_a \), smallest charge density anion
   \[ HF_{aq} \rightarrow H^+_{aq,F} + F^-_{aq} \quad K_a = 7.2 \times 10^{-4} \]
   c. Calculate how many protons omega gives up (equil)

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

\[ HF_{aq} \rightarrow H^+_{aq,F} + F^-_{aq} \quad K_a = 7.2 \times 10^{-4} \]

\[ H_2O \rightarrow H^+_{aq} + OH^-_{aq} \quad K_w = 10^{-14} \]

2. Excluding water, identify all the proton donors as

1. Strong acid
   a. Strong electrolyte: HNO₃, HCl, H₂SO₄ (No Clean Socks)
   No Strong Acids (SA)

2. Weak Acid
   a. Identify strongest acid (omega dog, can not hold protons)
   b. Has largest \( K_a \), smallest charge density anion
   \[ HF_{aq} \rightarrow H^+_{aq,F} + F^-_{aq} \quad K_a = 7.2 \times 10^{-4} \]
   c. Calculate how many protons omega gives up (equil)

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

\[ K_a = 7.2 \times 10^{-4} \]

\[ \text{Check assumptions} \]

\[ K_a = \frac{(x)(x + 10^{-7})}{1 - x} \approx \frac{x^2}{1 - x} = \frac{1}{1 - 7 \times 10^{-2}} \approx 1 \] Check assumptions

\[ l(K_a) = x^2 \]

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

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

\[ \text{Sig fig is here} \]

Calculate the pH of a solution of 1.00 M HF.

\[ K_a = 7.2 \times 10^{-4} \]

\[ \text{Sig fig is here} \]

\[ 0.983 = 1 \quad 0.0270001 = 0.027 \]
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)$_4^-$.

\[
B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad K_a = 5.8 \times 10^{-10}
\]

1. Write down ALL possible reactions involving a proton:
\[
B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H_3O^+ \quad K_a = 5.8 \times 10^{-10}
\]

2. Identify proton donors:
   1. strong acids: No Clean Socks?
   2. Weak acids: Students do This on your own

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

```
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$_2$SO$_4$, 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 HOC₆H₅. Calculate the conc. of -OC₆H₅ at this concentration.

1. Write down ALL possible reactions involving a proton
   \[ HF_{aq} + H_{aq}^+ F^- + H^+ \]
   \[ C_6H_5OH + H^+ \rightarrow C_6H_5O^- + H_2O \]
   \[ H_2O + H^+ \rightarrow OH^- + H^+ \]

2. Excluding water, identify all the proton donors as
   1. Strong acid
   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.**

\[
\begin{align*}
\text{HF} & \quad H^+ + F^- \quad K_a = 7.2 \times 10^{-4} \\
\text{HOC}_6\text{H}_5 & \quad H^+ + -OC_6\text{H}_5 \quad K_a = 1.8 \times 10^{-5} \\
\text{H}_2\text{O} & \quad H^+ + OH^- \quad K_w = 10^{-14}
\end{align*}
\]

\[
\begin{align*}
\text{stoic} & \quad 1 & \quad \text{n.a.} & \quad 1 & \quad 1 \\
\text{Init} & \quad 1.0 & \quad 0 & \quad 10^{-7} \\
\text{Change} & \quad -x & \quad +x & \quad +x \\
\text{Assume} & \quad 1.0 >> x & \quad x & \quad 10^{-7} < < x \\
\text{Equil} & \quad 1.0 & \quad x & \quad x
\end{align*}
\]

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

\[\sqrt{7.2 \times 10^{-4}} = x = 2.7 \times 10^{-2}\]

**Check assumptions:**
\[
\frac{2.7 \times 10^{-2} + 10^{-7}}{0.027} \approx 2.7 \times 10^{-2} ?
\]

\[
\frac{0.027}{0.00000001} = 0.0270001
\]

Sig fig = 1.0

---

**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; $K_{a2} = 1.2 \times 10^{-2}$

Pure Water

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>OH⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55.5</td>
<td>$10^{-7}$</td>
<td>$10^{-7}$</td>
</tr>
</tbody>
</table>

Control/complete H₂SO₄

<table>
<thead>
<tr>
<th>stoic.</th>
<th>H₂SO₄</th>
<th>HSO₄⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[init]</td>
<td>1</td>
<td>0</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>complete</td>
<td>0</td>
<td>0.0010</td>
<td>0.0010+10⁻⁷</td>
</tr>
<tr>
<td>stoic.</td>
<td>HSO₄⁻</td>
<td>H⁺</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>[init]</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>assume?</td>
<td>0.0010 &gt;x</td>
<td>0.0010 &gt;x</td>
<td>+x</td>
</tr>
<tr>
<td>[equil]</td>
<td>0.0010</td>
<td>0.0010</td>
<td>0.0010</td>
</tr>
</tbody>
</table>

Here is our first example in which we cannot make assumptions

\[
K_{a2} = 1.2 \times 10^{-2} = \frac{[\text{HSO}_4^-][\text{SO}_4^{2-}]}{[\text{H}_2\text{SO}_4]} \Rightarrow \frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{SO}_4]} = \frac{K_{a2}[\text{HSO}_4^-]}{[\text{SO}_4^{2-}]} = \frac{1.2 \times 10^{-2} \times 0.0010}{0.0010} = x
\]

Example: calculate the pH of 0.0010 M sulfuric acid; $K_{a2} = 1.2 \times 10^{-2}$

\[
x^2 + 0.013x - 1.2 \times 10^{-5} = 0
\]

\[
x = -0.013 \pm \sqrt{(0.013)^2 - 4(-0.0000012)}}{(2)}
\]

\[
x = -0.013 \pm \sqrt{2.17 \times 10^{-4}}
\]

\[
x = -\frac{0.013 \pm 0.0147}{2}
\]

- Solution gives a negative number which is not allowed

\[
x = 8.65 \times 10^{-4}
\]

$\text{[H}^+\text{]} = 0.001 + 0.000865 = 0.001865$

\[
\text{pH} = -\log(0.001865) = 2.73
\]

**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 HNO₂ using the iterative method (Kₐ=6.0x10⁻⁴)

<table>
<thead>
<tr>
<th>1 Pure Water</th>
<th>H₂O</th>
<th>OH⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>55.5</td>
<td>10⁻⁷</td>
<td>10⁻⁷</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>stoic.</th>
<th>HNO₂</th>
<th>NO₂⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Init]</th>
<th>0.100</th>
<th>0</th>
<th>10⁻⁷</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Change</th>
<th>-x</th>
<th>+x</th>
<th>+x</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Assume</th>
<th>0.100&gt;&gt;x</th>
<th>x</th>
<th>x&gt;&gt;10⁻⁷</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>[Equil]</th>
<th>0.100</th>
<th>x</th>
<th>x</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Calc 1</th>
<th>7.7x10⁻³</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>New Equil</th>
<th>0.100-7.7x10⁻³</th>
<th>x⁺⁺⁺⁺</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Calc 2</th>
<th>7.44x10⁻³</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>New New Equil</th>
<th>0.100-7.44x10⁻³</th>
<th>x⁺⁺⁺⁺⁺⁺</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Calc 3</th>
<th>7.45x10⁻³</th>
</tr>
</thead>
</table>

\[
K_a = \frac{c}{c^*} = \sqrt{K_a} \cdot \frac{c}{c^*} \cdot x
\]

\[
x^* = \sqrt{(6.0 \times 10^{-4})(0.1 - 7.7 \times 10^{-7})} = \sqrt{(6.0 \times 10^{-4})(0.0923)}
\]

\[
x = \sqrt{(6.0 \times 10^{-4})(0.1)} = 7.7 \times 10^{-3}
\]

\[
x^* = \sqrt{5.538 \times 10^{-3}} = 7.44 \times 10^{-3}
\]

Converging, plausible answer for iterative method: 0.100 M HNO₂, Kₐ=6.0x10⁻⁴

**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 (H₂SO₄, HSO₄⁻)
7. Triethylamine
8. NaAcetate
9. Our heme example

“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

Weak Bases
Calculation with Weak Base

Calc. the [OH], [H], and pH of 0.20 M solns of triethylamine, $K_b = 4.0 \times 10^{-4}$

<table>
<thead>
<tr>
<th></th>
<th>$H_2O$</th>
<th>$H^+$</th>
<th>$OH^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>stoic</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0.20</th>
<th>0</th>
<th>$10^{-7}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Init}]$</td>
<td>$-x$</td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>$\text{Assum}$</td>
<td>0.20</td>
<td>$x$</td>
<td>$10^{-7} &lt; x$</td>
</tr>
<tr>
<td>$\text{Equil}$</td>
<td>0.20</td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

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

$0.20 - 8.94 \times 10^{-3} = 0.2 \times 0.00894 \approx 0.00894$ Ronds to 0.0089

$pOH = -\log(0.00894) = 2.048$

$pH = 14 - 2.048 = 11.95$

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

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

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Module #17B: Acid Base Ionization Computations

Salts
Write all reactions involving protons, hydroxides

$Na(CH_3COO) + H_2O \leftrightarrow Na^+ + CH_3COO^-\text{aq}$

$CH_3COO^-\text{aq} + H_2O \leftrightarrow OH^-\text{aq} + CH_3COOH_{aq}$

$H_2O + Na^+ \text{aq} \rightarrow \text{no reaction}$

$H_2O \leftrightarrow H_3O^+ + OH^-\text{aq}$

$K_w = 10^{-14}$

Determine who is omega and will donate

$CH_3COO^-\text{aq} + H_2O \leftrightarrow CH_3COOH_{aq} + OH^-\text{aq}$

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? $K_a = 1.8 \times 10^{-5}$

$CH_3COOH_{aq} + H_2O \leftrightarrow CH_3COO^-\text{aq} + H_3O^+\text{aq}$

$CH_3COO^-\text{aq} + H_3O^+\text{aq} \leftrightarrow CH_3COOH_{aq} + H_2O\text{aq}$

$K_a = 1.8 \times 10^{-5}$

$1\over K_a = 10^{-14}$

$K_w = K_a K_b$

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

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? $K_a = 1.8 \times 10^{-5}$

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

$CH_3COO^-\text{aq} + H_2O \leftrightarrow CH_3COOH_{aq} + OH^-\text{aq}$

stoch 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? $K_a = 1.8 \times 10^{-5}$

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

$CH_3COO^-\text{aq} + H_2O \leftrightarrow CH_3COOH_{aq} + OH^-\text{aq}$

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? $K_a = 1.8 \times 10^{-5}$

$K_a = 5.55 \times 10^{-10}$
\[
\text{CH}_3\text{COO}^- + \text{H}_2\text{O} = \text{CH}_3\text{COOH} + \text{OH}^- \\
\text{stoich} \quad 1 \quad 1 \quad 1 \\
\text{[Init]} \quad 0.1 \quad 0 \quad 10^{-7} \\
\text{Change} \quad -x \quad +x \quad 10^{-7} + x \\
\text{Sum} \quad 0.1-x \quad 0+x \quad 10^{-7} + x \\
\text{Assume} \quad x << 0.1 \quad x \gg 10^{-7} \\
\text{[Equil]} \quad 0.1 \quad x \quad x \\
\text{Equil new} \quad 0.1-x \quad x \quad x + 10^{-7} \\
\]

\[
K_b = 5.55 \times 10^{-10} = \frac{[x][x + 10^{-7}]}{0.1 - x} = [x][x + 10^{-7}] = x^2 + (10^{-7})x \\
(5.55 \times 10^{-10})(0.1 - x) = [x][x + 10^{-7}] = x^2 + (10^{-7})x
\]

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? \( K_b = 1.8 \times 10^{-5} \)

---

Example Calculations
1. HCl
2. Acetic acid (vinegar)
3. HF
4. B(OH)\(_3\) (Boric acid (eye wash)) (students Do this one yourself)
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6. Mixture (H\(_2\)SO\(_4\), HSO\(_4^-\))
7. Triethylamine
8. NaAcetate
9. Our heme example

---

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Module #17B:
Acid Base Ionization Computations

Biological Chemistry

“A” students work (without solutions manual)
\~ 10 problems/night.
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 as having the most possible H bonds.

\[
\begin{align*}
K_{a,Val,COOH} &= 5.01 \times 10^{-3} \\
K_{a,Val,COOH} &= 5.01 \times 10^{-3} \\
K_{a,Val,COOH} &= 5.01 \times 10^{-3} \\
K_{a,Val,COOH} &= 5.01 \times 10^{-3}
\end{align*}
\]

\[
\begin{align*}
\text{Mass balance} & \quad \left[HA_{aq}\right] = \left[H_{a,eq}\right] + \left[A_{a,eq}\right] \\
\%\text{dissociated} &= \frac{\left[A_{a,eq}\right]}{\left[H_{a,eq}\right]} \times 100 \\
\%\text{dissociated} &= \frac{\left[A_{a,eq}\right]}{\left[H_{a,eq}\right] + [A_{a,eq}]} \times 100
\end{align*}
\]

\[
\begin{align*}
\text{Repeat procedure with tyrosine} & \quad \text{Hint: Want Val ionized, Tyr not ionized}
\end{align*}
\]
“A” students work (without solutions manual) ~ 10 problems/night.

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Module #17B: Acid Base Ionization Computations

We want to know when assumptions are valid.

<table>
<thead>
<tr>
<th>Init</th>
<th>HA(aq)</th>
<th>H⁺ from HA</th>
<th>A⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA_INIT</td>
<td></td>
<td>10⁻⁷</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil</td>
<td>HA_INIT-x</td>
<td>10⁻⁷ +x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_a = \left( \frac{x}{HA_{\text{init}}} \right) \approx \frac{x^2}{HA_{\text{init}}} = \frac{x}{HA_{\text{init}}} \]

\[ 100 \text{ < } 5\% \text{ ???} \]

\[ \% \text{ionized} = \frac{x}{HA_{\text{init}}} \times 100 \]

\[ \% \text{dissociated} = \frac{[A^-]}{[HA_{\text{aq}}]} \times 100 \]

\[ K_a = \frac{[A^-][H^+]}{[HA_{\text{aq}}]} \]

\[ % \text{dissociated} = \frac{\sqrt{K_a} [HA_{\text{aq}}]}{[HA_{\text{aq}}] + \sqrt{K_a} [HA_{\text{aq}}]} \times 100 \]

\[ K_a = \frac{[A^-][H^+]}{[HA_{\text{aq}}]} \]

\[ K_p = \frac{[H_2O][H^+][I^-]}{[HI]} \]

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 Cl₂ given that at 35 °C the equilibrium constant, K_c, is 1.6x10⁻⁵ mol/L?

Red herrings: 35 °C is a red herring!

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

Example 2: \( CO_2(g) + H_2O(g) \rightarrow CO_3^{2-}(aq) + H_2O(g) \) K_c is 0.64.

Example 3: \( N_2O_4(g) \rightarrow 2NO_2(g) \) K_c = 0.36M We will define Small in the Next chapter!

Example 4: \( H_2O(g) \rightarrow I_2(g) + 2HI(g) \) K_p is 1x10⁻².

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

Considering a simple system

\[ HA_{\text{aq}} \rightleftharpoons A^-_{\text{aq}} + H^+_{\text{aq}} \]

Mass balance

\[ [HA_{\text{aq}}] = [A^-_{\text{aq}}] + [H^+_{\text{aq}}] \]

\[ [A^-_{\text{aq}}] \leq \sqrt{K_a [HA_{\text{aq}}]} \]

\[ \% \text{dissociated} = \frac{[A^-_{\text{aq}}]}{[HA_{\text{aq}}] + \sqrt{K_a [HA_{\text{aq}}]}} \times 100 \]

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

Small $K \sim < 10^{-6}$
Sort of small $10^{-6} < K < 10^{-4}$
Large $K \sim > 10^{-3}$

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