**Makeup Midquarter Exams**
Wed., Mar 7
5:30-7:20 pm
1000 McPherson

You MUST Sign up in 100 CE
Please do so as soon as possible, but no later than Friday, Mar 2.

**Final Exams for Chem 122 - Mathews**
2:30 Class: Thursday, Mar. 15 at 1:30 in (TBA)
6:30 Class: Tuesday, Mar. 13 at 7:30pm in (TBA)

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**Quiz Number 4 – in lecture**
15 minutes, 20 pts

1. (4 pts) A salt solution is found to be neutral. Which of the following could be the salt(s) used to form the solution? KBr, NH4Cl, KCN, or K2CO3?

2. (10 pts) Calculate the [OH-] and pH for a solution that is 0.085 M in NaF. K_a (HF) = 6.8 x 10^-4

3. (6 pts) How would you rationalize the fact that:
   a. H2S is a stronger acid than H2O?
   b. H2SO4 is a stronger acid than HSO4-?

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**Types of Weak Bases**
- Bases generally have lone pairs or negative charges in order to attack protons.
- Most neutral weak bases contain nitrogen.
- Amines are related to ammonia and have one or more N-H bonds replaced with N-C bonds (e.g., CH3NH2 is methylamine).
- Anions of weak acids are also weak bases. Example: OCl- is the conjugate base of HOCl (weak acid):

\[
\text{ClO}^-_{(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{HClO}(aq) + \text{OH}^-_{(aq)} \quad K_b = 3.3 \times 10^{-7}
\]

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**Relationship Between K_a and K_b**
- We need to quantify the relationship between strength of acid and conjugate base.
- When two reactions are added to give a third, the equilibrium constant for the third reaction is the product of the equilibrium constants for the first two:

\[
\text{Reaction 1} + \text{reaction 2} = \text{reaction 3}
\]

has

\[
K_1 \times K_2 = K_3.
\]

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**Relationship Between K_a and K_b**
- For a conjugate acid-base pair

\[
K_a \times K_b = K_w
\]

- Therefore, the larger the K_a, the smaller the K_b. That is, the stronger the acid, the weaker the conjugate base.
- Taking negative logarithms:

\[
pK_a + pK_b = pK_w
\]
Consider the following interesting reaction:

\[ \text{HF} + \text{CN}^- = \text{HCN} + \text{F}^- \]

how do we get \( K = ?? \)

Given \( K_a(\text{HCN}) = 6.17 \times 10^{-16} \)
and \( K_a(\text{HF}) = 6.6 \times 10^{-4} \)

derive \( K \) for the above reaction.

\[ \text{Acid-Base Properties of Salt Solutions} \]

- Nearly all salts are strong electrolytes.
- Therefore, salts exist entirely of ions in solution.
- Acid-base properties of salts are a consequence of the reaction of their ions in solution.
- The reaction in which ions produce \( H^+ \) or \( OH^- \) in water is called hydrolysis.
- Anions from weak acids are basic.
- Anions from strong acids are neutral.
- Anions with ionizable protons (e.g. \( \text{HSO}_4^- \)) are amphoteric.

What happens if we put \( \text{NaOAc} \) in water?

\( \text{NaOAc(s)} \text{ in water} \Rightarrow \text{Na}^+ (\text{aq}) + \text{OAc}^- (\text{aq}) \text{ (100%) } \)

But what do we know about the acetate ion???

\[ \text{HOAc} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OAc}^- \text{ \( K_a = 1.8 \times 10^{-5} \)} \]
\[ \text{OAc}^- + \text{H}_2\text{O}^+ = \text{HOAc} + \text{H}_2\text{O} \text{ \( K = (K_a)^{-1} \)} \text{ and } \text{\( K = K_w \)} \]
\[ \text{i.e. OAc}^- + \text{H}_2\text{O} = \text{HOAc} + \text{OH}^- \text{ \( K = K_b = K_w(K_a)^{-1} \)} \]

Consider a 0.10 M solution of \( \text{NaCN} \), \( K_c = 4.0 \times 10^{-10} \)
calculate \([\text{OH}^-]\), \( pH \), and \% hydrolysis

Consider a 0.10 M solution of \( \text{NaOAc} \), \( K_c = 1.8 \times 10^{-5} \)
calculate \([\text{OH}^-]\), \( pH \), and \% hydrolysis

Likewise for

0.10 M \( \text{NiNic} \), \( K_c(\text{nicotinic acid}) = 1.4 \times 10^{-5} \)

0.10 M \( \text{NH}_4\text{Cl} \), \( K_b(\text{NH}_3) = 1.8\times10^{-5} \)

Consider a solution made with \( \text{NaOCl} \) in water to generate 2.00 L of solution with a \( pH=10.5 \). What is the number of moles of \( \text{NaOCl} \) dissolved in this soln?

Sample Exercise 16.18, p 702

What is the \( pH \) of a 0.10 M solution of \( \text{Na}_2\text{HPO}_4 \)?
\[ \text{H}_3\text{PO}_4: K_{a1}=7.5 \times 10^{-3}, K_{a2}=6.2\times10^{-8}, K_{a3}=4.2\times10^{-13} \]
Factors That Affect Acid Strength
Consider H-X. For this substance to be an acid we need:
• H-X bond to be polar with Hδ+ and Xδ- (if X is a metal then the bond polarity is Hδ-, Xδ+ and the substance is a base),
• the H-X bond must be weak enough to be broken,
• the conjugate base, X-, must be stable.

Binary Acids
• Acid strength increases across a period and down a group.
• Conversely, base strength decreases across a period and down a group.
• HF is a weak acid because the bond energy is high.
• The electronegativity difference between C and H is so small that the C-H bond is non-polar and CH₄ is neither an acid nor a base.

Oxyacids
• Oxyacids contain O-H bonds.
• All oxyacids have the general structure Y-O-H.
• The strength of the acid depends on Y and the atoms attached to Y.
  – If Y is a metal (low electronegativity), then the substances are bases.
  – If Y has intermediate electronegativity (e.g. I, EN = 2.5), the electrons are between Y and O and the substance is a weak oxyacid.
Oxyacids
- If Y has a large electronegativity (e.g. Cl, EN = 3.0), the electrons are located closer to Y than O and the O-H bond is polarized to lose H⁺.
- The number of O atoms attached to Y increase the O-H bond polarity and the strength of the acid increases (e.g. HOCl is a weaker acid than HClO₂ which is weaker than HClO₃ which is weaker than HClO₄ which is a strong acid).

Carboxylic Acids
- These are organic acids which contain a COOH group (R is some carbon containing unit):

\[
\text{R} - \text{C} - \text{O} - \text{H}
\]
- When the proton is removed, the negative charge is delocalized over the carboxylate anion:

\[
\begin{align*}
\text{R} - \text{C} - \text{O} & \quad \text{R} - \text{C} - \text{O}^- \\
\text{O}^- & \quad \text{O}^- \\
\end{align*}
\]
- The acid strength increases as the number of electronegative groups on R increases.

- Brønsted-Lowry acid is a proton donor.
- Focusing on electrons: a Brønsted-Lowry acid can be considered as an electron pair acceptor.
- Lewis acid: electron pair acceptor.
- Lewis base: electron pair donor.
- Note: Lewis acids and bases do not need to contain protons.
- Therefore, the Lewis definition is the most general definition of acids and bases.
- Lewis acids generally have an incomplete octet (e.g. BF₃).
- Transition metal ions are generally Lewis acids.
- Lewis acids must have a vacant orbital (into which the electron pairs can be donated).
- Compounds with π-bonds can act as Lewis acids:

\[
\text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{H}_2\text{CO}_3(aq)
\]
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### Quiz Number 4 – in lecture 15 minutes, 20 pts

1. (4 pts) Predict whether aqueous solutions of the following salts are acidic, basic, or neutral: KBr, NH₄Br, NaCN, or K₃PO₄?

2. (10 pts) Calculate the [OH⁻] and pH for a solution that is 0.068 M in NaClO. $K_a (HClO) = 3.0 \times 10^{-8}$

3. (6 pts) Based on their compositions and structures and on conjugate acid-base relationships, choose the stronger base in each of the following pairs:
   a. BrO⁻ or ClO⁻
   b. HCO₃⁻ or CO₃²⁻?

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### Hydrolysis of Metal Ions
- Metal ions are positively charged and attract water molecules (via the lone pairs on O).
- The higher the charge, the smaller the metal ion and the stronger the M-OH₂ interaction.
- Hydrated metal ions act as acids:
  
  Fe(H₂O)₆³⁺(aq) + H⁺(aq) \rightleftharpoons Fe(H₂O)₅(OH)²⁺(aq) + H⁺(aq) \quad K_a = 2 \times 10^{-3}

- The pH increases as the size of the ion increases (e.g. Ca²⁺ vs. Zn²⁺) and as the charge increases (Na⁺ vs. Ca²⁺ and Zn²⁺ vs. Al³⁺).

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### The hydrolysis of a cation

depends on the relative size and charge.

They tend to be acidic since the strong electron interaction tends to weaken the O-H bond.

Fe³⁺ → Fe(H₂O)₆³⁺ = Fe(H₂O)₅(OH)²⁺ + H⁺


Chapter 17.1

Common Ion Effect:

This is the same as other equilibrium calculations, except there is an initial concentration of two species prior to establishing equilibrium.

Consider a solution which is prepared by mixing 0.10 mole of acetic acid and 0.010 mole of HCl in enough water to make 1.00 L of solution.

What are the concentrations of each species?

Note that for a solution of 0.10 M acetic acid alone, [OAc⁻] = [H₃O⁺] = 1.3 x 10⁻³ M

Note, however, that we’re doing the same things again!

The expression \( K_a = \frac{[H_3O^+][A^-]}{[HA]} \) can be written\[
[H_3O^+] = K_a \cdot \frac{[HA]}{[A^-]}
\]
or the Henderson-Hasselbalch Equation(s)

Valid ONLY when [H₃O⁺] and [OH⁻] are very small in comparison to [A⁻] and [HA]ᵢ

Consider a solution made from dissolving 0.30 moles of acetic acid and 0.30 moles of sodium acetate in enough water to make 1.00 L of solution.

What is the concentration of Hydronium ions and the pH?

\[
\begin{align*}
\text{HOAc} + \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{OAc}^- \\
i &\quad 0.30 \text{ M} \quad \sim 0 \quad 0.30 \text{ M} \\
\delta &\quad -x \quad x \quad x \\
eq &\quad (0.30-x) \quad x \quad (0.30+x) \\
K_a &\quad 1.8 \times 10^{-5} = \frac{[x](0.30+x)}{[(0.30-x)]} \\
\text{leads to} \quad x &\quad = [H_3O^+] = 1.8 \times 10^{-6} \text{ M compared to} \\
2.3 \times 10^{-3} \text{ M} &\quad \text{for the acid alone!!!}
\end{align*}
\]

Now let’s add 0.10 mol of strong acid (eg HCl) to the solution (without changing its volume).

\[
\begin{align*}
\text{HA} &\quad \text{H}_3\text{O}^+ \quad \text{H}_2\text{O}^+ \quad A^- \\
i &\quad 1.00 \quad 0.500 \quad 0.010 \\
\delta &\quad -x \quad x \quad x \\
eq &\quad 1.00 + x \\
f &\quad 1.00 + x \\
\delta &\quad -x \quad x \\
e &\quad 0.500+x \\
f &\quad 0.500+x \\
\delta &\quad 0.10 \quad -x \\
\text{equ} &\quad 1.10 \quad = \\
\text{eq} &\quad 1.10 \quad x \\
\text{eq} &\quad 0.400 \\
\text{eq} &\quad 0.400 \\
\end{align*}
\]

And \( pH = -\log \left( \frac{0.400}{1.10} \right) = 3.75 + (-4.44) = 3.31 = \text{pH} \)

or [H₃O⁺] = 4.89 x 10⁻⁴

Consider 1.00L of solution containing 1.00 mol of formic acid (HCOOH) and 0.500 mol of sodium formate (NaHCOO). What is the pH? \( K_a = 1.77 \times 10^{-4} \)

Now let’s add 0.10 mol of strong acid (eg HCl) to the solution (without changing its volume).

i.e., we have made a BUFFERED solution.
A similar calculation results when we add enough strong base to the original buffer solution to make the solution 0.10 M in OH⁻.

<table>
<thead>
<tr>
<th></th>
<th>HA</th>
<th>H₂O</th>
<th>OH⁻</th>
<th>A⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>3.54x10⁻⁴</td>
<td>0.500</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>-x</td>
<td>-x</td>
<td>-x</td>
<td>0.10</td>
</tr>
<tr>
<td>net</td>
<td>-0.10</td>
<td>0.500</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In this case, [H₃O⁺] = 2.66x10⁻⁴ and pH = 3.58.