Acid-Base Equilibria
Chemwiki site: Chapter 12.2-12.7

1. Application of equilibrium concepts.
2. Not much else new in the way of theory is presented.
3. Specific focus on aqueous systems.
4. Assume we are at equilibrium unless otherwise specified.

I. Acids & Bases
A. General ideas:
   1. Some H nuclei are quite stable in their bonding arrangements.
      Example: The H nuclei in methane (CH₄) have almost zero tendency to leave their
      bonding e⁻ pair and go elsewhere.

      \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{no reaction} \]

B. Brønsted-Lowry Theory
   1. An acid is a substance that can donate a H⁺.
   2. A base is a substance that can accept a H⁺.

   Requires non-bonding e⁻ pair!!

   3. A general expression of an acid-base rxn.:

   \[ \text{HA} + \text{B} \rightleftharpoons \text{BH}^+ + \text{A}^- \]

   acid base acid base

   4. Specific expression:

   \[ \text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^- \]

   acid base acid base

C. Conjugates:
   a) Conjugate base is what is “leftover” after the acid has donated its H⁺.
   b) Conjugate acid is what “results” after the base has accepted its H⁺.

   \[ \text{HNO}_3 + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NO}_3^- \]

   Problems:
   a) Rxn. of CH₃COOH (acetic acid) with water:

   b) Rxn. of NH₃ (weak base) with water:
D. Acid Strength & Base Strength (context dependent!!!)

1. 1st, a qualitative approach to this subject. Then, a quantitative approach.

2. In this equation, H$_2$O is functioning as a base:

\[
\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^- (aq)
\]

Consider HA and H$_3$O$^+$ as two competing acids. Let’s look at which one is stronger?

First, what does an acid do? 

Does a strong acid do this better than a weak acid?

The stronger acid will be best at donating its H$^+$ ion.

So let us say HA is the stronger acid, will the rate of the forward reaction or reverse reaction be higher?

To which side will the equilibrium shift?

3. A relative strength picture:

\[
\text{HCl}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons
\]

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons
\]

When you dissolve 1 mole of HCl in 1 L of water, you will get a higher [H$_3$O$^+$] than when you do the same with CH$_3$COOH. Which is a stronger acid?

\[\text{Question: If HA is a strong acid, is its conjugate base strong or weak?}\]

\[\text{A brief aside:}\]

\[\text{When a H}^+ \text{ ion is released in water, it does not usually exist as a free H}^+ \text{ ion. It binds to water:}\]

\[\text{H}_2\text{O}^+ \text{ is called the hydronium ion.}\]

\[\text{H}_3\text{O}^2+, \text{H}_2\text{O}_2^+, \text{H}_6\text{O}_4^+, etc., likely exist as well.}\]

4. A quantitative approach to acid strength, $K_a$

a) Consider when a weak acid like acetic acid dissolves in water.
\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)
\]

There is a special name for the equilibrium constant when an acid dissolves in water; it is called an acid-dissociation constant, \(K_a\).

Can you write the \(K_a\) expression for:

\[
K_a =
\]

Remember about solids and liquids and \(K\)’s. \([\text{H}_2\text{O}]\) as the solvent does not change significantly.

c) The \(K_a\) value for \(\text{HCl}\) = ________________

The \(K_a\) value for \(\text{CH}_3\text{COOH}\) = ________________

Which is a stronger acid? \(\text{HCl}\) or \(\text{CH}_3\text{COOH}\)

E. The Dissociation of Water

1. Water is interesting. It can be both an acid and a base:

\[
\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)
\]

Lewis dot for water?

On your own, write this reaction using Lewis structures instead of molecular formulas.

2. Can we write a \(K_{eq}\) expression for the reaction of \(\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l)\) ? We call this \(K_w\)

\[
K_w =
\]

As you write the \(K_w\), remember about solids, liquids and \(K\)’s.

Also \([\text{H}_2\text{O}]\) as the solvent does not change significantly.

3. In “pure” water at 25°C, \([\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}\) M.

4. In “pure” water at 25°C, \([\text{OH}^-]\) = ______________ ?
5. What is \([H_2O] = \) ___________?

6. Now solve for value of \(K_w\): \(K_w = [H_3O^+] [OH^-]\)

**Problem:** If \([H_3O^+]\) for a solution = \(3.84 \times 10^{-9}\), what is \([OH^-]\)?

**II. The pH Scale (The power of Hydrogen)**

There are a bunch of reasons for using the pH, as opposed to \([H_3O^+]\). Convenience in expressing the numbers is probably most important to you.

A. By definition: \(pH = -\log [H_3O^+]\),

or a log of a number is the power you raise 10 to so that it equals the number.

1. With your calculator, enter 10, push log.
   \[
   \begin{align*}
   \log 10 &= \\
   \log 100 &= \\
   \log 0.001 &= 
   \end{align*}
   \]

   Convert 10, 100, 0.001 into scientific notation:
   \[
   \begin{align*}
   \log 10 &= \log (1 \times 10^1) = \\
   \log 100 &= \log (1 \times 10^2) = \\
   \log 0.001 &= \log (0.0001 \times 10^{-3}) = 
   \end{align*}
   \]

2. Let’s start with an example of pH.

*Calculate* the pH of a 1.0 \(\times\) 10\(^{-2}\) M solution of HBr, *(a strong acid).*

Note that as \([H_3O^+]\) increases, pH decreases.  
Logic: \(pH = \text{negative} \) log of \([H_3O^+]\).

B. How about the reverse of this process?  
What if you have the pH and you want to find the concentration of the H\(_3\)O\(^+\)*.
\[ [\text{H}_3\text{O}^+] = 10^{-\text{pH}} \]

Calculate \([\text{H}_3\text{O}^+] \& [\text{OH}^-]\) for a gastric juice sample with a \(\text{pH} = 2.09\).

C. What about rounding? (the × ÷ rule plus one?).

\[ -\log (1.0 \times 10^{-9}) = 9.00 \quad 1.0 \text{ has two sig fig} \]
\[ -\log (3.28 \times 10^{-5}) = 4.484 \quad 3.28 \text{ has three sig fig} \]

D. Why do we care about \(\text{pH}\)? (Review Apollo 13 clip?)

III. Acid-Base Buffers

A. Buffers function to limit change in \(\text{pH}\) when an acid or base is added to a system. Do you think the blood has buffers? (Several!)

B. A buffer is prepared by combining a weak acid with its conjugate base (in what ratio?)

For acetic acid/acetate, \(\text{CH}_3\text{COOH}\) combined with \(\text{CH}_3\text{COONa}\)

What happens to \(\text{CH}_3\text{COONa}\) when you dissolve it in water?

\[
\begin{align*}
\text{H}_2\text{O} & \\
\text{CH}_3\text{COONa} & \rightarrow
\end{align*}
\]

C. Acid part of the buffer neutralizes added base, while the base neutralizes added acid.

\[
\begin{align*}
\text{Added strong base} & \\
\text{CH}_3\text{COOH} + \text{OH}^- & \rightarrow
\end{align*}
\]

\[
\begin{align*}
\text{Added strong acid} & \\
\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ & \rightarrow
\end{align*}
\]

D. The Henderson-Hasselbalch Transformation

1. Can we rearrange the \(K_a\) expression to get an equation with \(\text{pH} = \ ?\)

Start with \(K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}\)
Finish with \[ \text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]} \]

Note: If pH = −log [H₃O⁺], what do you think pKₐ is?

\[ \text{p}K_a = \]

2. Why is the Henderson-Hasselbalch Transformation useful? **Buffers!**

   a) What would an ideal buffer contain?
   Lots of both HA (acid) and A⁻ (conjugate base).
   (example: CH₃COOH and CH₃COO⁻)

   b) Why?

   c) What happens to pH in the Henderson-Hasselbalch when [HA] = [A⁻]?
   (example: [CH₃COOH] = [CH₃COO⁻])
   Substitute [HA] = [A⁻] and simplify. What do you obtain?

   d) If the pH is lower than pKa (is more acidic)
   (without doing math),
   Then the concentration of HA (acid) is higher than the concentration of A⁻ (conj. base)
   (example: [CH₃COOH] > [CH₃COO⁻])

   e) If the pH is higher than pKa (is more basic)
   (without doing math),
   Then the concentration of HA (acid) is lower than the concentration of A⁻ (conj. base)
   (example: [CH₃COOH] < [CH₃COO⁻])

What does the results above mean in terms of most appropriate choice of weak acid to buffer at a given pH?

In practice, you want the pKa to be close, but certainly within 1 pH unit of the pH you want.

3. Looking from a Medical Perspective:
Your blood must be kept at a very constant pH!

(Proteins in your blood contain amino acids with acidic and basic groups. Altering the pH can affect whether the groups are in their acid or conjugate base form. This affects the interactions that hold the protein in its appropriate structure. If they lose their structure, they lose their function.)
Your blood has several systems to keep it constant.

1. Buffers

2.

3. One of the main buffers involves the weak acid, H$_2$CO$_3$
   It is formed when CO$_2$ reacts with H$_2$O.

\[ \text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \]

Which dissociation is physiologically relevant?

\[ \text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \quad pK_{a1} = 6.38 \]

\[ \text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad pK_{a2} = 10.32 \]

4. Let’s look at the Normal Values section of:

   (at sea level)

   \[ \text{pH} = 7.38 - 7.42 \]
   \[ P_a\text{CO}_2 = 38 - 42 \text{ mm Hg} \]
   \[ P_a\text{O}_2 = 75 - 100 \text{ mm Hg} \]
   \[ \text{SaO}_2 = 94 - 100\% \]
   \[ \text{HCO}_3^- = 22 - 28 \text{ mEq/L} \]

Which relate directly to acid-base chemistry?

Can you relate the terms to variables in the Henderson-Hasselbalch transformation?

\[ \text{pH} = pK_a + \log([A^-]/[HA]) \]

**Acidosis**, low blood pH, can result initially in light-headedness.
   If severe, it depresses the CNS and can lead to coma and death.

**Alkalosis**, high blood pH, causes headaches, nervousness, cramps.
   If severe it can lead to convulsions and death.