Acid-Base Concepts -- Chapter 16

1. Arrhenius Acid-Base Concept (last semester)

   **Acid:** H⁺ supplier  **Base:** OH⁻ supplier

2. Brønsted-Lowry Acid-Base Concept (more general)

   (a) Definition (H⁺ transfer)

   **Acid:** H⁺ donor  **Base:** H⁺ acceptor

   **Conjugate Acid-Base Pairs:**

   Base $\xrightleftharpoons{+ \text{H}^+}{- \text{H}^+}$ Acid

   e.g.,

   [conjugate pair]

   $\text{NH}_3$ + $\text{H}_2\text{O}$ $\rightleftharpoons$ $\text{NH}_4^+$ + $\text{OH}^-$

   \[\text{base} \quad \text{acid} \quad \text{acid} \quad \text{base}\]

   [conjugate pair]

   more examples:

   [conjugate acids]

<table>
<thead>
<tr>
<th>NH₂⁻</th>
<th>NH₃</th>
<th>NH₄⁺</th>
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<tbody>
<tr>
<td>OH⁻</td>
<td>H₂O</td>
<td>H₃O⁺</td>
</tr>
<tr>
<td>O²⁻</td>
<td>OH⁻</td>
<td>H₂O</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>H₂SO₄</td>
<td>H₃SO₄⁺</td>
</tr>
<tr>
<td>CH₃⁻</td>
<td>CH₄</td>
<td>&quot;CH₅⁺&quot;</td>
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   [conjugate bases]
(b) Amphoteric Substances -- molecules or ions that can function as both acids and bases (e.g., H₂O itself !)

- \text{HCO}_3^- + \text{OH}^- \longrightarrow \text{H}_2\text{O} + \text{CO}_3^{2-}

- \text{HCO}_3^- + \text{HCl} \longrightarrow \text{H}_2\text{CO}_3 + \text{Cl}^-

(c) Relative Strengths of Brønsted Acids

**Binary Acids**

- e.g., HCl, HBr, H₂S, etc.

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Binary Acids
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- Acid Strength Increases

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<table>
<thead>
<tr>
<th>Periodic Table</th>
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<tbody>
<tr>
<td>Acid Strength Increases</td>
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- e.g., relative acidity: HCl > H₂S (across a period)
- HI > HBr > HCl > HF (up in a group)
**Oxo acids**

e.g., HNO₃, H₂SO₄, H₃PO₄, etc.

1. *for same central element,*
   acid strength increases with # of oxygens

   Acid Strength Increases
   
   \[
   \text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4
   \]

2. *for different central element, but same # oxygens,*
   acid strength increases with electronegativity

   Acid Strength Increases
   
   Periodic Table

   e.g., H₂SO₄ > H₂SeO₄ > H₂TeO₄

(d) **Relative strengths of conjugate acid-base pairs**

For example,

\[
\begin{align*}
\text{HF} & + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ & + & \text{F}^- \\
\text{acid} & \text{base} & \text{acid} & \text{base}
\end{align*}
\]

In this case, the equilibrium lies mainly on reactant side. Therefore, "HF is a weaker acid than H₃O⁺"

In general, weak Brønsted acids have strong conjugate bases. (*vice versa*)
3. **Lewis Acid-Base Concept** (most general)

(a) **Definition** (electron pair transfer)

**Acid:** e⁻ pair acceptor  
**Base:** e⁻ pair donor

**Lewis acids** -- electron deficient molecules or *cations*.
**Lewis bases** -- electron rich molecules or *anions*.
(they have one or more unshared e⁻ pairs)

(b) **Lewis acid-base reactions** (i.e., all non-redox reactions!)

\[ \text{OH}^- + \text{NH}_4^+ \rightarrow \text{H}_2\text{O} + \text{NH}_3 \]

\[ \text{Lewis acids} \]

\[ \text{Lewis base} \]

\[ \text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^- \]
4. **Auto-ionization of Water and the pH Scale**

(a) water undergoes self-ionization to slight extent:

\[
\begin{align*}
H_2O + H_2O & \rightleftharpoons H_3O^+(aq) + OH^-(aq) \\
H_3O^+ & \text{ hydronium ion} \\
OH^- & \text{ hydroxide ion}
\end{align*}
\]

or, in simplified form:

\[
\begin{align*}
H_2O(l) & \rightleftharpoons H^+(aq) + OH^-(aq)
\end{align*}
\]

equilibrium constant:

\[
K_c = \frac{[H^+] [OH^-]}{[H_2O]}
\]

but, \([H_2O] \sim \text{constant} \sim 55.6 \text{ mole/L at 25°C}

so, instead, use the "ion product" for water = \(K_w\)

\[
K_w = [H^+] [OH^-] = 1.0 \times 10^{-14} \text{ (at 25°C)}
\]

in pure water: \([H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}\)

(b) **the pH scale:**

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

in general: \(pX = -\log X\)

e.g., \(pOH = -\log [OH^-]\)

and, in reverse:

\[
[\text{H}^+] = 10^{-pH} \text{ mole/L}
\]

\[
[\text{OH}^-] = 10^{-pOH} \text{ mole/L}
\]

since \(K_w = [H^+] [OH^-] = 1.0 \times 10^{-14}\)

\[
pK_w = pH + pOH = 14.00
\]
(c) relative acidity of solutions:

**neutral solution**

\[ [H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M} \]

\[ \text{pH} = \text{pOH} = 7.00 \]

**acidic solution**

\[ [H^+] > 10^{-7} \text{ (i.e., greater than in pure water)} \]

so, \[ \text{pH} < 7.00 \]

\[ [OH^-] < 10^{-7} \text{ and } \text{pOH} > 7.00 \]

e.g., if \[ [H^+] = 1.00 \times 10^{-3} \text{ M} \]
then \[ \text{pH} = 3.00 \text{ and } \text{pOH} = 11.00 \]

**basic solution**

\[ [H^+] < 10^{-7} \text{ (i.e., less than in pure water)} \]

so, \[ \text{pH} > 7.00 \]

\[ [OH^-] > 10^{-7} \text{ and } \text{pOH} < 7.00 \]

e.g., if \[ [OH^-] = 1.00 \times 10^{-3} \text{ M} \]
then \[ \text{pOH} = 3.00 \text{ and } \text{pH} = 11.00 \]

**Problem**

The water in a soil sample was found to have \[ [OH^-] \] equal to \[ 1.47 \times 10^{-9} \text{ mole/L} \]. Determine \[ [H^+] \], \text{pH}, \text{ and pOH} \]

\[ [H^+] = K_W / [OH^-] = (1.00 \times 10^{-14}) / (1.47 \times 10^{-9}) \]
\[ = 6.80 \times 10^{-6} \]

\[ \text{pH} = -\log [H^+] = -\log (6.80 \times 10^{-6}) = 5.17 \text{ (acidic !)} \]

\[ \text{pOH} = 14.00 - \text{pH} = 14.00 - 5.17 = 8.83 \]

\{ \text{or, } \text{pOH} = -\log [OH^-] = -\log (1.47 \times 10^{-9}) = 8.83 \}
5. **Strong acids and Bases**

(a) **Strong Acids** (e.g., HCl, HNO₃, etc.) -- 100 % ionized

\[
\text{HNO}_3(aq) + \text{H}_2\text{O} \xrightarrow{100\%} \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq)
\]

or, in simplified form:

\[
\text{HNO}_3(aq) \xrightarrow{100\%} \text{H}^+(aq) + \text{NO}_3^-(aq)
\]

\[[\text{H}^+] = \text{initial M of HNO}_3\]

e.g., in a 0.050 M HNO₃ solution:

\[[\text{H}^+] = 0.050 \quad \text{and} \quad \text{pH} = -\log (0.050) = 1.30\]

(b) **Strong Bases** (metal hydroxides) -- 100 % ionized

\[
\text{NaOH}(aq) \xrightarrow{100\%} \text{Na}^+(aq) + \text{OH}^- (aq)
\]

\[[\text{OH}^-] = \text{initial M of NaOH}\]

**Problem**

What mass of Ba(OH)₂ (171.34 g/mole) is required to prepare 250 mL of a solution with a pH of 12.50?

First: What is the solution process?

\[
\text{Ba(OH)}_2(aq) \xrightarrow{100\%} \text{Ba}^{2+}(aq) + 2\text{OH}^- (aq)
\]

so, \[[\text{OH}^-] = 2 \times \text{M of Ba(OH)}_2 \text{ solution} \quad (2:1 \text{ ratio})\]

\[
\text{pOH} = 14.00 - \text{pH} = 14.00 - 12.50 = 1.50
\]

\[[\text{OH}^-] = 10^{-1.50} = 0.0316 \text{ M}\]

Next: How much Ba(OH)₂ is needed for that much OH⁻?

250 mL \( \times \) \( \frac{0.0316 \text{ mol OH}^-}{1000 \text{ mL}} \) = 0.00790 mol OH⁻

0.00790 mol OH⁻ \( \times \) \( \frac{[1 \text{ mol Ba(OH)}_2 / 2 \text{ mol OH}^-]}{1 \text{ mol Ba(OH)}_2} \)

\( \times \) \( \frac{171.34 \text{ g}}{\text{mol Ba(OH)}_2} \) = 0.677 g
6. **Weak Acids and Bases**

(a) **Weak Acids -- less than 100% ionized (equilibrium !)**

in general: HA is a weak acid, $A^-$ is its conjugate base

\[
HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)
\]

or, in simplified form:

\[
HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)
\]

**Acid Dissociation Constant:** $K_a$

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

relative acid strength:

- weak acid: $K_a < ~ 10^{-3}$
- moderate acid: $K_a \sim 1$ to $10^{-3}$
- strong acid: $K_a >> 1$

**Problem**

Hypochlorous acid, HOCl, has a $pK_a$ of 7.52. What is the pH of 0.25 M solution of HOCl? What is the percent ionization?

\[
pK_a = -\log K_a
\]

\[
K_a = 10^{-pK_a} = 10^{-7.52} = 3.02 \times 10^{-8}
\]

\[
\begin{array}{cccc}
\text{HOCl(aq)} & \rightleftharpoons & \text{H}^+ & + & \text{OCl}^- (aq) \\
\text{Initial} & 0.25 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equil} & 0.25 - x & x & x
\end{array}
\]
now, substitute the appropriate equilibrium concentrations:

\[
K_a = [H^+] [OCl^-] / [HOCl] = 3.02 \times 10^{-8}
\]

\[
(x) (x) / (0.25 - x) = x^2 / (0.25 - x) = 3.02 \times 10^{-8}
\]

since \(K_a\) is very small, assume \(x << 0.25\)

\[
x^2 / (0.25) \approx 3.02 \times 10^{-8} \Rightarrow x \approx 8.69 \times 10^{-5}
\]

(assumption is OK)

\[
pH = - \log (8.69 \times 10^{-5}) = 4.06 \text{ (solution is acidic!)}
\]

% ionization = \((\text{amount HA ionized}) / (\text{initial}) \times 100\%\)

\[
= 100\% \times (8.69 \times 10^{-5}) / (0.25) = 0.035\%
\]

(b) Weak Bases

in general: B is a weak base, HB+ is its conjugate acid

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

**Base Dissociation Constant:** \(K_b\)

\[
K_b = [\text{HB}^+] [\text{OH}^-] / [\text{B}]
\]

e.g., NH3 is a weak base:

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

\[
K_b = [\text{NH}_4^+] [\text{OH}^-] / [\text{NH}_3] = 1.8 \times 10^{-5}
\]

\[
pK_b = - \log K_b = 4.74
\]

**Note:** Since OH\(^-\) rather than H\(^+\) appears here, first find [OH\(^-\)] or pOH, and then convert to pH

sample problem: 0.25 M solution of NH3

set up conc table as usual, solve for \(x = [\text{OH}^-]\)

\[
[\text{OH}^-] = 2.12 \times 10^{-3}
\]

\[
pOH = 2.67 \quad \text{pH} = 11.33 \quad \text{(basic!)}
\]
7. **Salts of Weak Acids and Bases**

(a) **Conjugate Acid - Base Pairs** *(HA and A\(^-\))*

\[ \begin{align*}
K_a & : \quad HA \quad \rightleftharpoons \quad H^+ \quad + \quad A^- \\
K_b & : \quad A^- \quad + \quad H_2O \quad \rightleftharpoons \quad HA \quad + \quad OH^- 
\end{align*} \]

for any conjugate acid-base pair:

\[ K_a \times K_b = K_w \quad \text{and} \quad pK_a + pK_b = 14.00 \]

(b) **Salt of a Weak Acid** *(e.g., NaCN) -- Basic Solution*

Anion acts as a weak base:

\[ \begin{align*}
K_b & : \quad CN^- \quad + \quad H_2O \quad \rightleftharpoons \quad HCN \quad + \quad OH^- \\
K_b & = \frac{K_w}{K_a} = \frac{[OH^-][HCN]}{[CN^-]} \\
e.g., & \quad K_a \text{ for HCN is } 6.2 \times 10^{-10} \\
\text{what is pH of a } 0.50 \text{ M NaCN solution?} & \\
K_b & = \frac{K_w}{K_a} = \frac{(1 \times 10^{-14})}{(6.2 \times 10^{-10})} \\
& = 1.6 \times 10^{-5} \\
\text{use a concentration table based on } K_b \text{ reaction above:} & \\
x & = [OH^-] = [HCN] \\
[CN^-] & = 0.50 - x \approx 0.50 \quad \text{(since } K_b \text{ is small)} \\
K_b & = [OH^-][HCN]/[CN^-] \approx x^2 / 0.50 \approx 1.6 \times 10^{-5} \\
x & = [OH^-] \approx 2.8 \times 10^{-3} \\
pOH & = 2.55 \quad \text{and} \quad pH = 11.45 \quad (\text{basic!})
\]
(c) Salt of a Weak Base (e.g., NH₄Cl) -- *Acidic Solution*

Cation acts as a weak acid:

\[ \text{K}_a:\quad \text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3 \]

\[ \text{K}_a = \frac{\text{K}_w}{\text{K}_b} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \]

e.g., \( \text{K}_b \) for NH₃ is \( 1.8 \times 10^{-5} \)

what is pH of a 0.50 M NH₄Cl solution?

\[ \text{K}_a = \frac{\text{K}_w}{\text{K}_b} = \frac{(1 \times 10^{-14})}{(1.8 \times 10^{-5})} \]
\[ = 5.56 \times 10^{-10} \]

use a concentration table based on \( \text{K}_a \) reaction above:

\[ x = [\text{H}^+] = [\text{NH}_3] \]

\[ [\text{NH}_4^+] = 0.50 - x \approx 0.50 \quad \text{since \( \text{K}_a \) is small} \]

\[ \text{K}_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \approx \frac{x^2}{0.50} \approx 5.56 \times 10^{-10} \]

\[ x = [\text{H}^+] \approx 1.67 \times 10^{-5} \]

\[ \text{pH} = 4.78 \quad \text{(acidic !)} \]

**Problem**

The \( \text{pK}_a \) value for HCN is 9.21. What molar concentration of NaCN is required to make a solution with a pH of 11.75? [answer: 2.0 M NaCN]
8. **Polyprotic Acids**

e.g., diprotic acids, $H_2A$, undergo stepwise dissociation:

$$H_2A \rightleftharpoons HA^- + H^+ \quad K_{a1} = [HA^-][H^+] / [H_2A]$$

$$HA^- \rightleftharpoons A^{2-} + H^+ \quad K_{a2} = [A^{2-}][H^+] / [HA^-]$$

usually, $K_{a1} \gg K_{a2}$ so that:

- the 1st equilibrium produces most of the $H^+$
- but, the 2nd equilibrium determines $[A^{2-}]$

**Problem**

Ascorbic acid (vitamin C), $H_2C_6H_2O_6$, is an example of a diprotic acid with $K_{a1} = 7.9 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$. For a 0.10 M solution of ascorbic acid, determine the pH and the concentrations of the mono anion, $HC_6H_2O_6^-$, and the dianion, $C_6H_2O_6^{2-}$.

based on the first equilibrium:

$$x = [H^+] = [HA^-] \quad \text{and} \quad [H_2A] = 0.10 - x \approx 0.10$$

$$K_{a1} = 7.9 \times 10^{-5} \approx x^2 / (0.10)$$

$$\therefore x \approx 2.8 \times 10^{-3} \quad \text{so,} \quad \text{pH} = 2.55$$

must use the 2nd equilibrium to find $[A^{2-}]$:

$$K_{a2} = [A^{2-}][H^+] / [HA^-] \quad \text{but, from above} \quad [H^+] \approx [HA^-]$$

$$\therefore K_{a2} \approx [A^{2-}] \quad \text{(a general result for } H_2A \text{!)}$$

$$[A^{2-}] \approx 1.6 \times 10^{-12}$$