Week 15/Tu: Lecture Units 36, 37

Unit 35: Equilibrium Constants

Unit 36: Aqueous solutions
-- Electrolytes, Equilibria
-- Acid/Base Definitions

Unit 37: Acid/Base, pH
-- Acid / Base Conjugates
-- Definition of pH

Unit 38: Hydrolysis
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Issues: Last Week of Classes, Course Evaluations today

LAST Homework Set 11 due on Saturday @ 08:00AM
The final exam is a *common final* and has been scheduled for Thursday, December 13th 7:45 - 9:45AM

The exam will have < 40 questions, cumulative, for a total of 250 pts.

There will be an alternate final exam for anyone who has EITHER:
1) another final scheduled at the same time as our final OR
2) three or more finals on Thursday (i.e., two others plus our final)

The alternate exam will be given the day before (Wed. at 10am)

Sign-up for the alternate this week in Room 185 Gen. Chem. Office
On-line, University Wide:

Student Opinion of Courses and Teaching (SOCT) collects student feedback on courses and instruction at MSU. Rating information collected by SOCT is reported in summary form only and cannot be linked to individual student responses. Student anonymity is carefully protected. You should have received an e’mail message with instructions. If you have any questions, please contact Sandra Walther, (swalther@msu.edu).

Printed Form, Chemistry Dept.:

You will have the opportunity to fill out a scan-tron form at the end of class today that is collected by the Chemistry Dept. and the results will be given to me sometime next semester.
Quite some time ago we looked at the different categories of solutions, now we want to look in depth into the very important aqueous solutions.

<table>
<thead>
<tr>
<th>General Solution</th>
<th>Aqueous</th>
<th>Degree of Ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute</td>
<td>non-electrolyte</td>
<td>weak</td>
</tr>
<tr>
<td>Solute</td>
<td>electrolyte</td>
<td>slight</td>
</tr>
<tr>
<td>Solvent</td>
<td>water</td>
<td>complete</td>
</tr>
</tbody>
</table>

The most important electrolytes in chemistry are acids and bases.

We now know that the ionization process, like any other chemical process, should be viewed as an equilibrium. Last week we introduced equilibrium constants and we can use that approach to describe the behavior of electrolytes in solution.
Previously we didn’t always write down the complete chemical equation for the equilibrium of electrolytes in water. Now, for example:

\[ \text{HCl (g) } + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq) } + \text{Cl}^- \text{ (aq)} \quad K_{EQ} = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}][\text{H}_2\text{O}]} \]

We previously identified HCl as a strong acid – the equilibrium for this reaction lies on the “product” side.

\[ K_A(\text{HCl}) = K_{EQ} *[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{Cl}^-]}{[\text{HCl}]} \]

Other Strong electrolytes listed in the Notes that we have come across already include:

-- all salts (product of reactions between acids & bases)
-- the strong acids: HCl, HClO\textsubscript{4}, HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}
-- the strong bases: NaOH, etc., Ca(OH)\textsubscript{2}, etc.

We expect all of these equilibria to lie “far to the right” as written, but note that it is an “equilibrium” and we would expect some reactant left, even if it was a very, very small amount.
The weak electrolytes have the opposite behavior. For example (only one letter different from the previous case :-)

\[
\text{HCN (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{CN}^- (aq) \quad K_{\text{EQ}} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}][\text{H}_2\text{O}]} 
\]

We previously identified HCN as a weak acid – the equilibrium for this reaction lies on the “reactant” side.

\[
K_A(\text{HCN}) = K_{\text{EQ}} \cdot [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}
\]

Other Weak electrolytes listed in the Notes that we have come across already include:
-- weak acids: CH₃CO₂H, (and other organic acids) HF, HNO₂
-- weak bases: NH₃ (NH₄OH) more on this one later

We expect all of these equilibria to lie “far to the left” as written. Note, again, that this is an equilibrium and we would expect some product to be present even if it is a small amount.
Over time the definition of what is an acid and what is a base has shifted and has become more general. We will consider the three major definitions of acids and bases. They go by the names of the classifiers:
\( (A, B-L, L) \):

**Arrhenius:** (Classic definition that you already know) for Aqueous Soln.
Acid – increases the concentration of \( H_3O^+ \) ions of water in solution
Base – increases the concentration of \( OH^- \) ions of water in solution

\[
\begin{align*}
\text{HCl (g) + H}_2\text{O (l)} & \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{Cl}^- (aq) \\
\text{NaOH (s) + H}_2\text{O (l)} & \rightleftharpoons \text{Na}^+ (aq) + \text{OH}^- (aq)
\end{align*}
\]

Combine an Arrhenius Acid & Base – neutralization

Net Reaction: \( H_3O^+ (aq) + OH^- (aq) \rightleftharpoons 2 \text{H}_2\text{O (l)} \)

Spectator Ions: \( \text{Na}^+ (aq), \text{Cl}^- (aq) \)
Over time the definition of what is an acid and what is a base has shifted and has become more general. We will consider the three major definitions of acids and bases. They go by the names of the classifiers: (A, B-L, L):

**Brønsted-Lowry:** a more general definition based on H exchange, always come in pairs, two pair to make a reaction.

Brønsted-Lowry Acid – a compound that donates a proton (H\(^+\))
Brønsted-Lowry Base – a compound that accepts a proton

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

Each acid/base “pair” is easy to identify because one partner has one more proton (H\(^+\) including the charge) than the other one.
Over time the definition of what is an acid and what is a base has shifted and has become more general. We will consider the three major definitions of acids and bases. They go by names of the classifiers: (A, B-L, L):

**Brønsted-Lowry:** a more general definition based on H exchange, always come in pairs, two pair to make a reaction.

**Brønsted-Lowry Acid** – a compound that donates a proton (H⁺)
**Brønsted-Lowry Base** – a compound that accepts a proton

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

This is a little unusual reaction that we will have to come back to next time, called “hydrolysis” and occurs with the salts of weak elect.
Over time the definition of what is an acid and what is a base has shifted and has become more general. We will consider the three major definitions of acids and bases. They go by names of the classifiers:

(A, B-L, L):

**Lewis:** the most general definition based on (you guessed it) electron pairs:
- Lewis Acid – a compound that accepts an electron pair in a reaction
- Lewis Base – a compound that donates an electron pair in a reaction

\[
\text{H}^+ (\text{aq}) + :\text{O}-\text{H}^- (\text{aq}) \iff \text{H}_2\text{O} (\text{l})
\]

The donation of the pair of electrons does not always form a strong chemical bond, particularly in Boron or Aluminum compounds (empty orbital for these Group 13 / IIIA elements).

\[
\text{BF}_3 (\text{g}) + :\text{NH}_3 (\text{g}) \iff \text{F}_3\text{B}:\text{NH}_3
\]
**Brønsted-Lowry**: the general definition based on H exchange, always come in pairs. The “acid” form has the extra proton.

Examples from the *Notes*

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>(one less H(^+))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{SO}_3)</td>
<td>(\text{HSO}_3^-)</td>
<td></td>
</tr>
<tr>
<td>(\text{HCN})</td>
<td>(\text{CN}^-)</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{PO}_4^-)</td>
<td>(\text{HPO}_4^{2-})</td>
<td></td>
</tr>
<tr>
<td>(\text{H}_2\text{CO}_3)</td>
<td>(\text{HCO}_3^-)</td>
<td></td>
</tr>
<tr>
<td>(\text{HCO}_3^-)</td>
<td>(\text{CO}_3^{2-})</td>
<td></td>
</tr>
</tbody>
</table>
Week 15/Tu: Relative Strength of Acid/Base Pairs

Brønsted-Lowry: We can create a *Hierarchy by Strength* by simply putting the acid-form into water and observing the equilibrium (e.g. $K_A$)

$\text{HClO}_4 (aq) + H_2O (l) \leftrightarrow H_3O^+ (aq) + \text{ClO}_3^- (aq)$  ALL GO – far-right

$\text{H}_2\text{CO}_3 (aq) + H_2O (l) \leftrightarrow H_3O^+ (aq) + \text{HCO}_3^- (aq)$  equil – slightly right

$\text{NH}_4^+ (aq) + H_2O (l) \leftrightarrow H_3O^+ (aq) + \text{NH}_3 (aq)$  NO GO – far left

$\text{H}_3\text{PO}_4 (aq) + H_2O (l) \leftrightarrow H_2\text{PO}_4^- (aq) + H_3O^+ (aq)$  equil – slightly left

### Acid | Base | $K_A$
---|---|---
HClO$_4$ | HClO$_3^-$ | 3x10$^9$
HNO$_3$ | NO$_3^-$ | 2x10$^1$
H$_3$O$^+$ | H$_2$O | 7x10$^{-3}$
H$_3$PO$_4$ | H$_2$PO$_4^-$ | 2x10$^{-5}$
CH$_3$CO$_2$H | CH$_3$CO$_2^-$ | 6x10$^{-10}$
NH$_4^+$ | NH$_3$ | 2x10$^{-16}$
H$_2$O | OH$^-$ | $\sim$10$^{-30}$

Special Reference case, water!

$\text{H}_2O (l)+\text{H}_2O (l) \leftrightarrow \text{H}_3O^+ (aq) + \text{OH}^- (aq)$